ENVIRONMENTAL PROGRESS
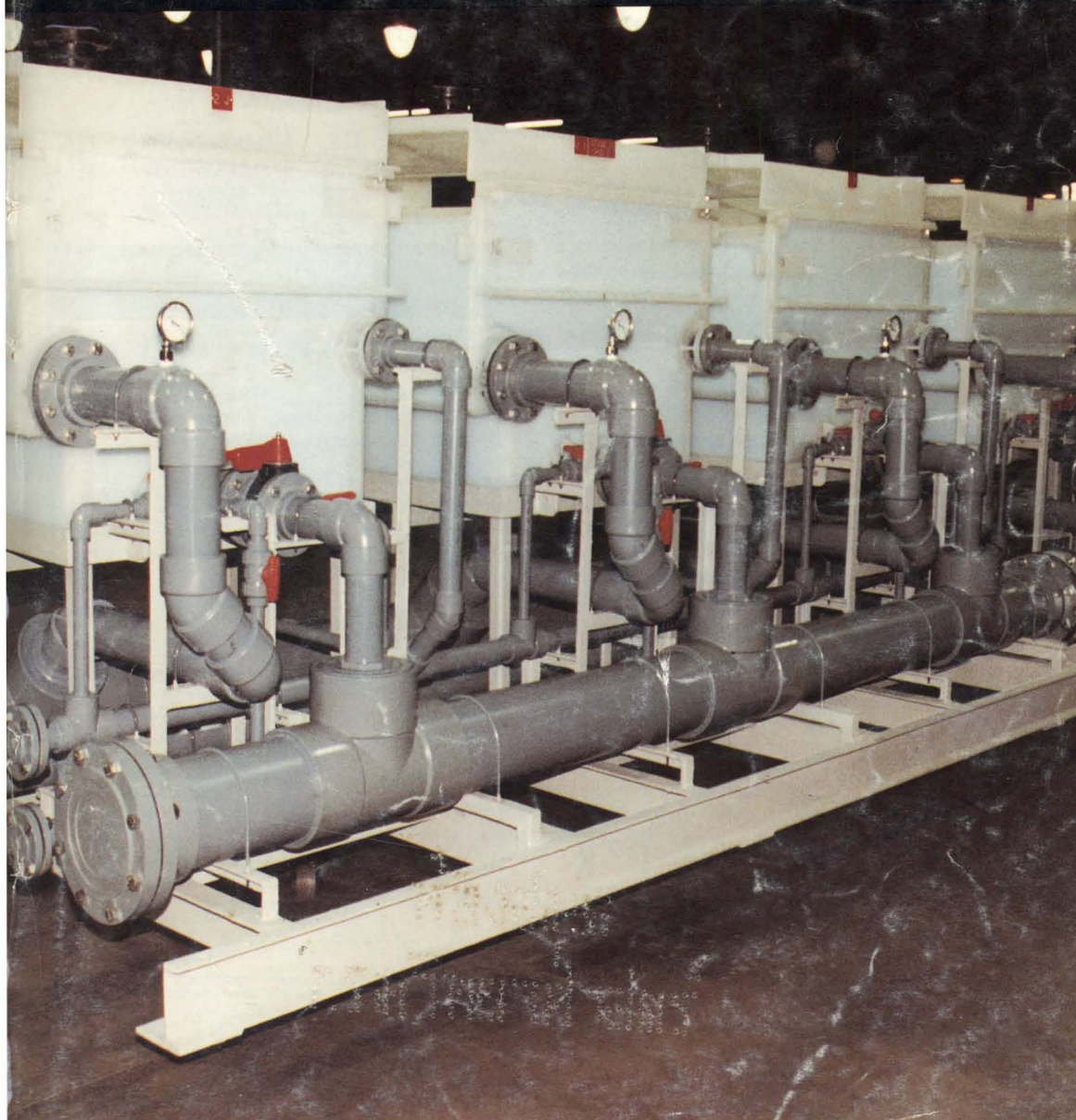
Environmental Considerations in Process Design and Simulation

Prepared by J. Eisenhauer and S. McQueen, Energetics Inc.

The Environmental Protection Agency, The Department of Energy, and The Center for Waste Reduction Technologies, presents a publication which identifies how environmental factors should be incorporated into process simulation and design tools for the chemical process industries.

Authored by leading U.S. experts drawn from the industrial user community, software designers, university researchers, and federal R&D managers—this publication identifies the important R&D needed in the process simulation area and offers some perspective on R&D priorities. Ideas range from new theoretical modeling approaches being pursued in the academic community to the pragmatic data needs of process engineers who must find ways to meet environmental regulations for current operating facilities.

Issues and R&D needs addressed:

- The pertinent environmental considerations and how they should be brought into the optimization/design process
- New process models or modifications required to accommodate environmental factors in process simulation
- Current concepts of process simulators and design tools modified to incorporate environmental factors
- Data required to support process simulation and design with environmental factors

Nearly all of the recommended R&D activities are expected to produce significant results within ten years. And nearly half of the R&D activities proposed will provide results in three years or less.

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Cover: Electrolyzers used in wastewater treatment (see article on page 122). Photo courtesy of Eltech Research Corporation, Fairport Harbor, Ohio.

ENVIRONMENTAL PROGRESS

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WASTEWATER

HAZARDOUS WASTE

Cleaning Up Superfund

J. Winston Porter

Porter Environmental, 211 Loudoun St., S.W., Leesburg, VA 22075

Subcommittees in the U.S. Senate and House of Representatives have proposed comprehensive new laws to fix the troubled Superfund waste site cleanup program. Some proposed changes, particularly those for the remedy selection process, are important steps in the right direction.

These reforms, however, do not go far enough in taking advantage of the success story right under our noses — the superfund-type programs of over 40 states. Briefly, many of the state programs are cleaning up sites at a fraction of the time and cost of the federal Superfund activity.

From most perspectives, Superfund has been a big disappointment. The EPA has spent about $15 billion on hazardous waste sites since 1980, with only about 250 of the current 1,300 Superfund sites actually cleaned up. A recent estimate places total annual Superfund sites actually cleaned up. A recent estimate places total annual Superfund spending at about $4 billion, with cleanup and non-cleanup (mostly legal) costs about equal.

The national program has emphasized cleanup regulations and procedures over cost-effectiveness and actual results. Average site cleanup costs are about $30 million, with site cleanups taking over 10 years. In contrast, in 1980, $1.6 billion was estimated to be sufficient to remediate about 400 sites, or about $4 million per site.

In addition to the cost issue, the Superfund program is often perceived as "unfair". Criticisms are aimed at such concepts as retroactive and joint and several liability, as well as enforcement against contributors of very small amounts of waste and even innocent landowners.

For a wide variety of political and other reasons, lawmakers are reluctant to grasp a clear, low-risk alternative: takeover of Superfund by the states. This reluctance exists even in the face of overwhelming evidence that states are cleaning up sites much faster and at less cost than the federal program.

For example, Minnesota cleanups normally take two to three years and cost less than $5 million. New York, California, and Wisconsin have all remediated more than 200 sites, about the same as the entire federal total of sites completed.

The states are doing well because waste sites are local problems commonly affecting a few dozen to a few hundred acres. These sites present issues which are very different from air or surface water pollution problems which often impact entire regions of the country.

A key component of the federal program has been the concept of "national consistency" in site remedies. That approach ignores the fact that each hazardous waste site is a unique problem. Some examples:

- In Florida, local groundwaters were contaminated by septic tanks serving numerous small industries.
- At Love Canal (where it all began) thousands of tons of chemicals were found in the midst of a residential area.
- At a rural Texas airport, pesticide washings from crop duster planes polluted some soil.

Due to these one-of-a-kind circumstances, solutions must be based on local environmental, land use, economic, and community concerns.

Very importantly, states have also been more innovative because they are less subject to Congressional micromanagement. Two of many examples:

- The State of Minnesota found that municipal landfills containing hazardous wastes were a particularly troublesome problem. Under Superfund, most of the "cleanup activity" was actually legal as hundreds of parties, including small municipalities, began to sue each other. In response, the state decided to take over the remediation of 106 closed municipal waste landfills in order to emphasize cleanup, not litigation.
- The California EPA introduced a streamlined, voluntary program to get contaminated properties back to productive use. Corporations, developers, and local and state agencies are now able to restore properties quickly and efficiently, without waiting for mandated cleanups.

The bills proposed in Congress have many of the elements which will be needed to fix Superfund, but they also include the tendency to introduce new federal complexities in an attempt to satisfy diverse groups of constituents.

The amended Superfund statute should make it attractive for most states to operate their own cleanup programs under their own laws and regulations. With states as the major players in a new Superfund, much of the expense and complexity associated with the old Superfund could be avoided.

Dr. J. Winston Porter is president of the Waste Policy Center in Leesburg, Virginia. He was assistant administrator of EPA with responsibility for the Superfund and RCRA programs from 1985 to 1989. He received his B.S. in chemical engineering from the University of Texas at Austin and his Ph. D. in the same field from the University of California at Berkeley. Dr. Porter is a member of AIChE.

W. WESLEY ECKENFELDER WINS THE LAWRENCE K. CECIL AWARD

W. Wesley Eckenfelder has been named as winner of the AIChE Environmental Division's 1996 Lawrence K. Cecil award. The award recognizes outstanding chemical engineering contributions and achievement in the preservation or improvement of the environment.

Recognized as one of the formost authorities on industrial water quality management, Eckenfelder has been responsible for the development of many treatment processes and design principles used throughout the world. He has authored 24 books, and more than 200 scientific papers.

After spending the early part of his career working for various universities and engineering firms, he formed Eckenfelder, Inc., a consulting firm in Nashville, Tennessee, in 1970 and served as president and chairman. That same year, he also joined the faculty of Vanderbilt University as a distinguished professor of environmental and water resources engineering. In 1989 he was named an emeritus distinguished professor of Vanderbilt and chairman emeritus of Eckenfelder Inc.

The holder of 15 awards from national and international societies for his contributions, Eckenfelder was founding member and president of the International Association for Water Pollution Research. He has served on 33 international committees and advisory boards, and has initiated and conducted numerous training courses in addition to consulting for more than 100 major US corporations.

Eckenfelder earned a BCE in civil engineering and a DSc honorary doctorate from Manhattan College, and an MS from The Pennsylvania State University and MCE from New York University, both in sanitary engineering. He also did postgraduate studies in chemical engineering at North Carolina State University. He is a registered professional engineer in Texas.

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The IDEA database developed by EPA's Office of Enforcement and Compliance Assurance provides new public access to new data and information. This data analysis tool, Integrated Data for Enforcement Analysis, allows the user to tap into a number of databases and retrieve information easily and quickly. The data can then be applied to insopection targeting, case screening, litigation support, settlement negotiations, and management decision making.

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IDEA is available by subscription from the National Technical Information Service. To order IDEA access, call the NTIS Subscriptions Department, 703-487-4630. *The IDEA User's Guide Book*, PB96-141569KAO ($49 plus handling fee) and the *IDEA Basic Training Course: Student Booklet*, PB96-780507KAO ($21.50 plus handling fee) may be ordered separately. Call NTIS Sales Desk, 703-487-4650. FAX orders to 703-321-8547. Rush service is available for additional fee, call 1-800-553-NTIS.

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Methods for Monitoring Pump-and-Treat Performance. This report was developed on behalf of EPA to outline methods of evaluating the effectiveness and efficiency of pump-and-treat remediation systems. Quote order number PB95-125456KAI, $25 plus handling fee.

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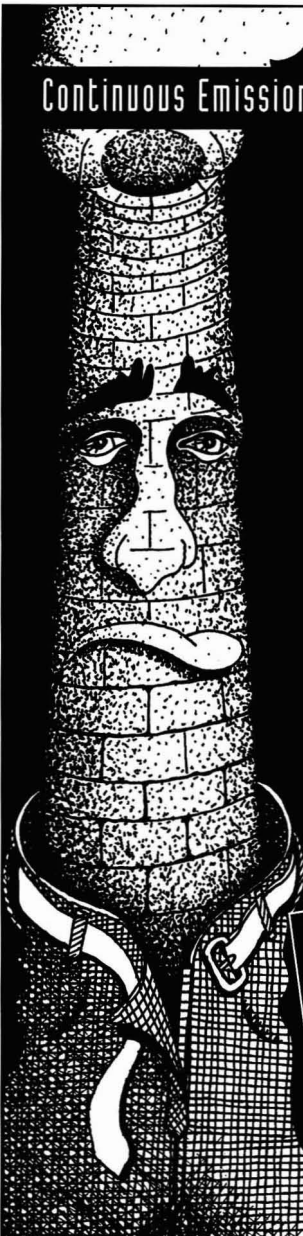
AIChE's Center for Waste Reduction Technologies (CWRT) recently published a monograph *How to Implement Industrial Water Reuse: A Systematic Approach.* The book shows how to systematically incorporate the principles of water conservation, recycling and reuse into new plant, retrofit and technology development design.

Reducing mineral waste is one of the greatest challenges facing industry today. Until now no guide existed to help conceptual process designers and process operators incorporate water reuse principles into plant operations.

"This timely publication is a practical "how to" guide and provides a systematic approach with outstanding examples from diverse industries" according to Jack Waaver, director of CWRT. He went on to say "using this publication as a guide, readers will easily be able to implement this practical approach in their industrial settings."

The information was drawn from literature reviews, surveys of industrial practices and the knowledge base of CH_2M Hill.

To order this publication ($40 prepaid) please call the AICHE*xpress* Service Center at 1-800-242-4363.

Superfund Reform Returns to Congressional Agenda

Prepared by AIChE's Government Relations Staff:
Dale E. Brooks and Sean Devlin Bersell

After months of backroom discussions and negotiations, Superfund reform has once again moved back on the congressional agenda. In March, Sen. Bob Smith (R-NH) released a comprehensive substitute to his Superfund reform bill (S. 1285). The Senate Environment and Public Works Committee held hearings on the Smith bill in late April, and the committee leadership hopes to approve the substitute bill this Spring. Over in the House, the full Commerce Committee appears to be moving toward approval of the Superfund bill (H.R. 2500), authored by Rep. Mike Oxley (R-OH), that was approved by the Commerce, Trade, and Hazardous Materials Sub-committee in November. A comparison of some of the key provisions of the two bills appears on the following pages.

Advocates for Superfund reform are anxious to have the House Commerce and Senate Environment committees approve the bills soon, as the bills must also be examined and approved by other committees in both the House and the Senate prior to floor action in each chamber. The shortened legislative year occasioned by the November general election leaves little margin for delay if a Superfund bill is to be enacted this year.

RESULTS-ORIENTED CLEANUPS

Both the Smith substitute and the Oxley bill include provisions embracing the "results-oriented approach" to Superfund cleanups advocated by the American Institute of Chemical Engineers. AIChE's results-oriented approach envisions compressing the multiple Superfund study processes into a single engineering study and identifying and implementing a remedy in a timely manner.

The Smith bill explicit directs EPA to pursue results-oriented cleanups so the response activities can reduce as quickly as possible the risks to human health and the environment. The Oxley bill contains a similar provision that would direct the President to consider new procedures, including a results-oriented approach, for conducting remedial investigations and feasibility studies. AIChE informed Congress that it believes the version in the Smith bill is preferable because it allows the results-oriented cleanups approach to be applied to all phases of Superfund cleanups and because it requires EPA to develop procedures for utilizing the results-oriented approach.

RESPONSE ACTION CONTRACTORS

The Smith and Oxley bills both would provide liability relief for response action contractors. The Superfund law and EPA's associated guidance expose response action contractors to Superfund liability even though response action contractors are not responsible for site contamination. This is believed to drive up the cost of cleanups as response action contractors seek to avoid liability by practicing "defensive engineering" and avoiding innovative technologies. The bills would seek to address this situation by excluding response action contractors from the definition of "owner and operator" for Superfund liability and establishing negligence as the standard of liability for actions undertaken by response action contractors.

SUPERFUND TAXES

The federal government's authority to collect the four Superfund taxes expired at the end of last year. The Superfund program is supported by taxes on petroleum, hazardous chemicals, and imported substances made with hazardous chemicals and the corporate environmental income tax. Renewal of the taxes, although widely supported, has been blocked by the lack of a comprehensive agreement by Congressional Republicans and the President of a plan to balance the federal budget.

(Continued overleaf)

Comparison of Superfund Reform Proposals of Sen. Smith and Rep. Oxley

Issue	Smith Bill (S. 1285)	Oxley Bill (H.R. 2500)
Community Involvement	Creates community response organizations to provide consultation throughout the response action process and to assist in determining future land uses.	Creates community response organizations to provide consultation throughout the response action process and to assist in determining future land uses.
State Delegation	Permits states to request full delegation of cleanup authority, utilizing State liability and remedy selection procedures.	Allows states to receive delegation of cleanup authority, utilizing federal liability and remedy selection procedures.
State Involvement in NPL Listings	Provides states with the authority to veto the addition of any site to the NPL and to delist sites.	Prohibits new NPL listings without the concurrence of the state and the local jurisdiction and allows states with delegated authority to delist sites if they determine no further action is necessary or a site cleanup will be conducted under RCRA or an enforceable agreement.
NPL	Allows EPA to add a total of 75 sites to the NPL over 7 years, and then caps the NPL.	Allows EPA to add a total of 75 sites to the NPL over 7 years, and then caps the NPL.
Site Delisting	Expedites delisting of a site once construction of the selected remedy is complete.	No provision.
Emergency Response	Extends the duration of emergency response activities to 24 months and increases the cost ceiling for such activities to $4MM per site.	Extends the duration of emergency response activities to 24 months and increases the cost ceiling for such activities to $3MM per site.
Voluntary Cleanups/Brownfields	Provides up to $25MM per year for State voluntary cleanups at non-NPL sites. Provides grants and loans for voluntary cleanups of abandoned industrial sites that could be redeveloped except that they are contaminated with hazardous materials ("brownfields").	Provides technical assistance to states to establish and expand voluntary cleanups.
Prioritization	basis of threats to human health and the environment.	Places a priority on cleaning up facilities with releases of hazardous substances that result in actual, ongoing human exposures at levels of public health concern.

Comparison of Superfund Reform Proposals of Sen. Smith and Rep. Oxley (cont.)

Issue	Smith Bill (S. 1285)	Oxley Bill (H.R. 2500)
Risk Assessments	Mandates site-specific risk assessments, wherever possible, based on actual or plausible exposure pathways that account for future land and water use. Where site-specific data is unavailable, the risk assessments are to use an acceptable range and distribution of realistic and plausible default assumptions.	Mandates site-specific risk assessments, wherever possible, that provide the best estimates of risks, based on all relevant information, and that indicate the reasonable range of uncertainty. Where site-specific data is unavailable, the risk assessments may be based on the most plausible assumptions.
Preferences for Permanence and Treatment and ARARs	Eliminates the preferences for permanence and treatment. Permits ARARs to be applied.	Eliminates the preferences for permanence and treatment and ARARs.
Cleanup Flexibility	Directs that all options for addressing contamination at a site be considered, including removal, containment, treatment, institutional controls, point-of-use treatment, natural attenuation, or a combination thereof, recognizing the limitations of currently available technology.	Directs that all options for addressing contamination at a site be considered, including containment, stabilization, treatment, institutional controls, source control, point-of-use treatment, provision of alternative water supply, natural attenuation, or a combination thereof, recognizing the limitations of currently available technology.
Remedy Selection	Requires EPA to select the most cost-effective remedy that protects human health and the environment. Establishes an acceptable risk range of 10^{-4} to 10^{-6} for human health.	Establishes an objective of protection of human health and the environment from realistic and significant risks through cost-effective and cost-reasonable means. Establishes an acceptable risk range of 10^{-4} to 10^{-6} for human health. The remedy selection process is to consider reasonably foreseeable future land and water use. The administering agency is to certify that the chosen remedy is cost-effective and that the incremental cost of the chosen alternative is reasonably related to the incremental risk reduction benefits.
Remedy Selection Factors	Directs that the following factors be balanced when determining the appropriate remedy: effectiveness; cost; reliability; short-term risks; technical feasibility; and community acceptance.	Directs that the following factors be considered in determining the appropriate remedy: effectiveness; reliability; implementation risks; community acceptance; and reasonableness of cost.

Comparison of Superfund Reform Proposals of Sen. Smith and Rep. Oxley (cont.)

Issue	Smith Bill (S. 1285)	Oxley Bill (H.R. 2500)
Generic Remedies	Directs EPA to develop technically practical and cost-effective presumptive remedies for commonly encountered facilities with well-understood contamination problems and exposure potentials.	Provides authority to establish generic or presumptive remedies for certain circumstances.
ROD Look-back	Creates an independent technical board to review existing RODs and make recommendations for alternative remedies if the new remedy selection standards would result in a lower-cost remedy.	Permits existing RODs to be reopened to determine if the new remedy selection standards would result in a lower-cost remedy that is protective of human health and the environment.
Remediation Wastes	Creates a new category of wastes, "remediation wastes," for media and debris generated by cleanups. The wastes would be subject to a special set of management requirements.	Creates a new category of wastes, "remediation wastes," for media and debris generated by cleanups. The wastes would be subject to a special set of management requirements.
Liability	Establishes a mandatory, non-binding "fair-share" allocation process for future response costs. Exempts generators and transporters at multi-party sites from pre-1981 liability. Provides liability exclusions and limitations for de minimus and de micromis parties and innocent purchasers, adjacent landowners, lenders, and lessors. The aggregate liability of generators and transporters of municipal solid waste and sewage sludge at a site would be capped at 10%. Orphan shares would be paid from the superfund.	Establishes a non-binding "fair-share" allocation process for future response costs. Allows PRPs at multi-party sites to be reimbursed from the Superfund for up to 50% of their future response costs for pre-1987 disposal. Provides liability exclusions and limitations for municipal landfills, oil recycling sites, battery recycling sites, de minimus and de micromis parties, and innocent purchasers, adjacent landowners, and lenders. The aggregate liability of generators and transporters of municipal solid waste and sewage sludge at a site would be capped at 10%. Orphan shares would be paid from the superfund.
Response Action Contractors	Limits the liability of response action contractors by clarifying that "owner and operator" does not include response action contractors and requiring that negligence be determined in light of generally accepted standards and practices in effect at the time.	Limits the liability of response action contractors by requiring that negligence be determined in light of generally accepted standards and practices in effect at the time.

Comparison of Superfund Reform Proposals of Sen. Smith and Rep. Oxley (cont.)

Issue	Smith Bill (S. 1285)	Oxley Bill (H.R. 2500)
Natural Resource Damages	Eliminates non-use damages and limits recovery to that necessary to restore the resource to the condition that would have existed if contamination had not occurred. Prohibits recovery for injuries resulting from releases before 1980.	Limits natural resource liability to the costs of restoration measures necessary to restore the resource to the condition that would have existed if contamination had not occurred and lost public use. Caps natural resource damages at $50MM per site. Prohibits recovery for injuries resulting from releases before 1980.
Federal Facilities	Permits qualified states to be delegated authority at Federal facilities.	Permits qualified states to be delegated authority at Federal facilities.
Superfund Taxes	Reauthorizes the taxes on petroleum, hazardous chemicals, and imported substances made with hazardous chemicals and the corporate environmental income tax.	Reauthorizes the taxes on petroleum, hazardous chemicals, and imported substances made with hazardous chemicals and the corporate environmental income tax.

BIOSURFACTANTS

Naim Kosaric, editor, Marcel Dekker,
Inc., New York, NY. (1994), 483 pages
[ISBN No.: 0-8247-8811-7], U.S. List
Price: $175.00.

The title of this book is an accurate description of the content of this volume. Naturally occurring surface active agents, i.e., emulsifiers, are essential to metabolic processes in many species. The managed behavior of these compounds can contribute to enhanced rate and/or quantitative efficiency of bioremediation of soils and water. Seventeen chapters are devoted to production, properties, and applications of complex biochemicals with substituents that couple hydrophobic and hydrophilic properties within the same molecule. Part 1 is a narrow, sophisticated description of Biochemistry Process Design and Engineering. Within the context of current practices for *in-situ* bioremediation and *ex-situ* biological treatment, the material presented is highly specialized and of peripheral interest to results-oriented scientists and engineers. In the broader context of pharmaceutical manufacturing and drug administration, basic biochemistry can contribute to higher reaction rates, more direct down-stream separation and purification, and more effective utilization.

Chapter 1 is an extensive overview of the basic biochemistry of biosurfactants. The literature review is extremely extensive, but lacks significant numbers of recent citations, i.e., 1990s. It is not certain whether this bibliography is timely. Subchapter III.A discusses n-alkane transport and three models for the process. The models are deemed to be preliminary and incomplete. Subchapter II.B discusses alkane oxidation; the goal of this chapter is furthered by the high quality of Figures 7 and 8. In general, Chapter 1 is aimed at specialists. Figures are of key importance and are of uneven quality, i.e., Figures 16, 17, and 19 are excellent, and Figure 18 is poor. Subchapter III is readable and Figure 6 is very informative.

Chapter 2 is entitled "Production of Biosurfactants". It is disappointing; it does not discuss production, as understood by process engineers. The reference section contains a greater number of current citations than Chapter 1; it represents a step toward timeliness. The citation of a "glycolipopeptide capable of emulsifying water-immiscible organophosphorus pesticides" on page 73 is attention-getting, but requires amplification. This may be a critical issue to "best management practice" for agriculture and rainfall runoff from agricultural and horticultural activities. Discussion of agitation speeds and shear effects (on page 81) is not consistent; the work of D.I.C. Wang warrants more extensive consideration. That the "oxygen transfer from gas to liquid is known to be affected by surfactants" is not surprising (see p.81 also). Why is this issue not examined in greater depth?

Chapter 3 deals with the important topic of whole-cell immobilization. The title is somewhat misleading, i.e., the text deals only with Rhamnolipids, not biosurfactants in general. Actually, this constraint is helpful. These extracellular metabolites appear to be an ideal basis for demonstrating the process concept. Discussion of production from immobilized bacteria is thorough and suited to self-learning or formal teaching. The figures and tables are well conceived and executed. Data for fluidized bed design and operation are an effective illustration of process application.

Chapter 4 is a case study; production refers to biochemical mechanism rather than an engineering process. Chapter 5 compliments Chapter 3 and does so in a meaningful fashion. The two chapters should have been placed together. The figures and tables are clear and contain very useful information; Table 2 is a nice summary of experimental results. Subchapter II.C on Gas Exchange stresses the importance of separation in a severely foaming system. Chapter 6 is an interesting biochemical survey that does not relate well to the other chapters of Part I, Chapter 7 is a collection of brief, applied case studies of glycolipid production.

Part II of the book is a series of five short chapters on biochemical and biophysical properties of biosurfactants. Chapter 8 describes genetic coding and transferability of enzyme capability; this chapter is a literature review, through 1991. Brief citations of crude oil degradation, in Subchapter II.A, and alkane utilization, in Subchapter II.B, do not contribute materially to the understanding of bioremediation. Chapter 9 summarizes data on biosurfactant toxicity and inhibitory effects on growth and activity. Data is taken from original sources, as identified.

Chapter 10 is a clear, concise review of fundamental thermodynamics of interfaces. It includes original, informative graphics and data calculated for microbial systems. Basic theory applies to gas/liquid, liquid/liquid, gas/solid, and liquid/solid interfaces. The use of the term "Biophysics" in the chapter title is fully justified; illustrations include cell distribution, cell surface energies, and cellular adhesion. Chapter 11 is a well-written, well illustrated discussion of respiratory physiology. It is interesting reading, but does not relate closely to the other chapters of the book. Chapter 12 is a highly specialized review; many citations seem outdated and too many citations have been taken from a single [voluminous] source. This chapter is a patchwork of materials from the scientific literature. The figures and tables are uniformly well executed; Figures 9 and 10 are especially weak.

Part III of the book is devoted to application. The title of Chapter 13 ("Factors Influencing the Economics of Biosurfactants") is attention-getting. However, the chapter does not deliver process economics; it is merely a review of speculative literature that points to the enormous importance of organism and substrate specific costs and benefits. Figures 9 and 11 are hypothetical and speak only to generalities of economic analyses. Note, biosurfactant synthesis and use are emerging technologies that constitute a volatile and competitive business arena; nonetheless, material included in this chapter is too general to be useful. Chapter 14 on Biosurfactants for cosmetics, is a business-to-business directory, with emphasis on the Japanese industry. No obvious purpose is served by the information contained in this chapter. Chapters 13 and 14 stress future developments; both chapters are lean on accomplishments and actual process-specific economic data.

Chapter 15 is a comprehensive discussion on the applied biochemistry of interactions of microorganisms with crude oil constituents in the marine environment. This chapter summarizes an extensive literature review of laboratory investigations relating to crude oil spills on the coasts of Israel, France, and Germany. The role of biosurfactants in emulsification of crude oil components is stressed; however, information on subsequent bioremediation of dispersed contaminants is included. The chapter will be of interest to chemical environ-

mental engineers with an interest in the marine environment.

Chapter 16 is not strictly devoted to the Application of Biosurfactants in the Food Industry. Section II is a first-rate review of the basic thermodynamics and physics of emulsions and interfaces. Formation, stability, and destabilization of emulsions are discussed with thoroughness and clarity. The title is inappropriate and may discourage potential interested users of the chapter contents. Although the graphics are reproductions from primary sources, they are well done and communicate effectively.

Chapter 17 is devoted to environmental applications. Section II draws heavily on the pioneering work of Atlas and Bartha; Figures 1 through 3 describe pathways for microbial degradation of n-alkanes, benzene, and catechol taken from that work. Section III is a brief discussion of biodegradation of crude oil at sea. This is not correlated with Chapter 15; lack of integration is a serious deficiency. Table 1 is outdated and irrelevant. Sections II and III do not make reference to biosurfactants. Section IV briefly summarizes two applications of biodegradation, in Canada and the United Kingdom. Several literature citations in this section are dated and speculative. Section V discusses laboratory studies of biosurfactants; Sections VI and VII are overly brief and vague.

The quality of this book is uneven. Several of the chapters are summaries of a massive literature; however, much of the book is directed toward scientific specialists. Chapters 10, 15, 16, and 17 are of interest to chemical environmental engineers. In addition, Chapters 3 and 5 will be of great interest to practitioners and teachers of biochemical engineering. Because of the unevenness of presentations, lack of editorial organization, inappropriate identification of subject matter, and an unusually high price, the book does not qualify as a personal reference for other that a limited number of biosurfactant specialists. However, it contains material that justifies use as a reference and source book for a variety of scientists and engineers. It should and will appear in may academic and industrial libraries.

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CANCER CHEMOTERAPEUTIC AGENTS

William O. Foye; Editor, American Chemical Society, Washington, D.C. (1995), 698 Pages, [ISBN No.: 0-8412-2920-1], U.S. List Price: $149.95

This book is a review of cancer chemotherapy, major accomplishments, and emerging areas of research in this important field. It is organized into 17 chapters based on the general mechanisms of actions of the various agents: (1) Introduction and historical background, (2) Prediction of biochemical mechanism of action from the *in vitro* antitumor screen of the National Cancer Institute, (3) Antimetabolites, (4) Agents that react with DNA, (5) Topoisomerase II inhibitors, (6) Inhibitors of DNA-transcribing enzymes, (7) Camptothecin and analogues: Synthesis, biological *in vitro* and *in vivo* activities, and clinical possibilities, (8) DNA minor-grove binding compounds as antitumor agents, (9) Antimitotic agents, (10) Bleomycin-group antitumor agents, (11) Drugs that block steroid hormone action for the treatment of breast and prostate cancer, (12) Photochemically activated anticancer agents, (13) Immune-modifying agents, (14) Hypoxia-selective cytotoxins, (15) Chemical radiation sensitizers and protectors, (16) Oligonuclides and polynucleotides as potential cancer chemotherapeutic agents, and (17) Antitumor antibiotics.

The book deals with each class of cancer chemotherapeutic agent and their development. Chapter 1 is an introduction and discusses the development of the various classes of agents through "rational" and "empirical" approaches, although not discounting the importance of serendipity in the process of drug discovery.

Chapter 2 on the prediction of biochemical mechanism of action from the *in vitro* antitumor screen of the National Cancer Institute (NCI), is an analysis of the NCI *in vitro* data base that answers questions that could not be asked in previous screening programs. The use of the COMPARE software program has enabled the identification of novel chemical structure classes exhibiting a biochemical mechanism in common with that established for known compounds. Also, the converse use of the software has allowed the identification of agents whose antitumor activity is mechanically unrelated to that of any known drug and may provide even

greater avenues to chemotherapeutic research.

Chapter 3 on antimetabolites discusses the following classes of compounds: fluorpyrimidines, thiopurines, inhibitors of nucleoside diphosphate reductase, 2'- deoxyribonucleoside analogues, other nucleosides, folic acid analogues, methotrexate and related diaminogeterocycles, 6-diazo-5-oxo-L-norleucine, L-asparaginase, and N-(phosphonoacetyl)-L-aspartic acid. The chapter begins with a general description of the antimetabolites. Each section often includes discussions of the chemistry, mechanisms of action, pharmacokinetics, toxicity, and new directions.

Chapter 4 discusses agents that react with DNA and includes the following classes of compounds; nitrogen mustard and related structures, platinum complexes, nitrosoureas, alkyl sulfonates, triazenylimidazoles, other triazenes, and imidazo[5,1-d]-1,2,3,5-tetrazin-4 (3H)-ones, aziridines, procarbozine, and hexamethylmelamine. The nitrogen mustards were the first clinically effective cancer chemotherapeutic agents, and the mechanisms of action of the antimetabolites and agents that react with DNA are compared at the beginning of the chapter. The pharmacology, clinical uses, mechanisms of action, toxicity, development of resistance, and the modulation and tumor activity and combination therapy are discussed.

Chapter 5 discusses topoisomerase II inhibitors under the following headings: inhibitors of DNA topoisomerases, role of intercalation and DNA binding in the activity of acridines and related tricyclic DNA-intercalating agents, and epipodophyllotoxins, aminoanthraquinones, ellipticine, merbarone, benzisoquinolinediones, and related compounds.

Chapter 6 is a listing and brief discussion of DNA-transcribing enzymes and the following processes: DNA-drug interaction via intercalation, transcription of DNA, a transcription and replication of RNA and DNA in viruses, inhibitors of transcription, inhibitors of prokaryotic RNA polymerase, inhibitors of eukaryotic RNA polymerase, rifamycins, and actinomycins. Discussions of their history, chemistry, biological properties, clinical uses, and pharmacokinetics are included.

Chapter 7 discusses comptothecin and analogues: synthesis, biological *in vitro* and *in vivo* activities, and clinical possibilities. Structural activity relationships, the effect of substituents on bio-

logical activities, stereochemistry, and clinical prospects are reported.

Chapter 8 discusses DNA nonintercalating minor-groove binding compounds as antitumor agents and includes distamycin and netropsin as prototypes. The discussion points to the fact that many of the nonintercalating minorgroove binding molecules show a marked preference for AT base pairs and marrow minor groove that occurs in the AT-rich regions of B-DNA.

Chapter 9 on antimitotic agents discussed: tubulin and microtubules and the drugs that interact with them, and drugs acting at the vinblastine and the colchicine sites. These agents are reported to be the most clinically useful drugs for cancer chemotherapy. Their toxic side effects, which are the major obstacles in the treatment of cancer with these agents are discussed, as are the mediators of the resistance to these drugs.

Chapter 10 on bleomycin (BLM)-group antitumor agents discusses the following: naturally occurring BLM-group antibiotics, semisynthetic and synthetic BLMs, BLM models, BLM as an antitumor agent, BLM-mediated DNA strand scission, and RNA strand scission by Fe-BLM.

Chapter 11 deals with drugs that block steroid hormone actions for the treatment of breast and prostate cancer. For breast cancer, the mechanisms of action of antiestrogens, and inhibitors of steroid biosynthesis are discussed. For prostate cancer, the mechanisms of action of nonsteroidal antiandrogens flutamide, casodex, anandron are discussed, along with the inhibitors of steroid biosyntheses finasteride and ketoconazole.

Chapter 12 deals with photochemically activated anticancer agents and their use in photodynamic therapy of superficial bladder cancer, esophageal, endobronchial and other cancers. Mechanisms of actions, structure activity relationships, and other applications of photoactivated drugs are presented.

Chapter 13 is a discussion of immune modifying agents. It contains an overview of the immune system, cellular and humoral immunity and their role in antitumor immunity, regulation of the immune response, the role of cytokines in immunity, immunological abnormalities in cancer, and immune modifying agents.

Chapter 14 talks about hypoxia-selective cytotoxins (HSCs). The chapter discusses the phenomenon of tumor hypoxia, resistance of hypoxic cells to conventional chemotherapy, hypoxic cells as a target for chemotherapy, design requirements for bioreductibly activated HSCs, mitomycin C, and other aziridoquinones, nitro aromatics that undergo internal rearrangement, dual function nitro aromatics, nitro aromatic deactivated mustards, N-oxides, metal complexes, and other triggering functions.

Chapter 15 discusses the chemical radiation sensitizers, nitroimidazoles, other nitroaryl compounds, RSU-1069, and other alkylating radiosensitizers, nitroxyl and N-oxides, halogenated pyrimidine analogues, and the radiation protector WR-2721.

Oligonucleotides and polynucleotides as potential cancer chemotherapeutic agents are discussed in Chapter 16. The focus of this chapter is on the new types of potential chemotherapeutic agents that have been developed on the basis of the idea of antitemplates, antimessengers, and antigenes.

Chapter 17 reports on antitumor antibiotics, with discussions on mithramycin and other aureolic acids, mitomycins, streptozocin, benzonapththopyranones, bisintercalators, CC-1065 and related compounds, distamycin and netropsin, ciynenes, napththyridinomycin, cyanocyclines, quinocarcin, nucleoside antibiotics, pyrrolo [1,4] benzodiazepines, saframycins, renieramycins, safracins, streptonigrins, and lavendamycin.

This book provides an excellent summary of the state of the art of the weapons in the arsenal of the toxicologist. It provided information on the advantages and limitations of the various modalities for cancer chemotherapy, giving, details o the chemistry, pharmacokinetics, clinical uses, clinical and preclinical toxicity, and specific target organs which are the most sensitive to each of the agents. The book is recommended as an excellent reference for both the researchers and clinicians involved with the development and/or therapeutic application of anticancer drugs.

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METAL SPECIATION AND CONTAMINATION OF SOIL

This book discusses metal speciation and contamination of soil from theoretical, experimental and pragmatic perspectives. It is based on a Workshop on Metal Speciaton and Contamination of Soils held at Jekyll Island, Georgia, on May 22-24, 1991. It includes articles describing the basic concept and/or recent research developments in the area of metal speciation, redox chemistry, kinetics of metal reactions, spectroscopic characterization of metal ion reactions, modeling hydrologic transport phenomena of metals, and remediation alternatives.

This book is recognized into 13 chapters written by a variety of experts from the United States and the other countries including Austria, Canada, China and Germany. The papers were written by 32 authors/coauthors primarily from academia, with several national laboratories/research centers, the U.S. Environmental Protection Agency, and private consulting firms also represented.

Chapter 1 presents a global perspective and defines the magnitude of the overall problem. The sources and transport of metal pollutants and their implications on human health are discussed. A good overview of metal sorption kinetics in soils is presented in Chapter 2. The mechanisms and kinetics of chemical processes that influence metal transport in soils are outlined in Chapter 3. Chapter 4 discusses the mechanisms of metal sorption onto the surface of oxide colloids. The significance and importance of substance colloidal transport of both bound-metal contaminants, and the transport of organic and inorganic colloids, are evaluated.

Chapter 5 reviews principals of redox reactions in soils and sediments, and their effects on metal transport. Chapter 6 discusses the metal immobilization, mineralization and remobilization at bacterial surfaces and at clay mineral-bacterial cell wall composite surfaces. Chapter 7 presents parameterizing coupled chemistry transport models for

understanding and predicting trace metal chemicals in groundwater. Chapter 8 deals with methodological problems involved in assessing metal mobility in soils.

Chapter 9 examines the use of water molecules and metal cations as molecular probes to study the surface chemistry of smectite-water interactions. Experimental results for treating the soils contaminated with heavy metals using several chelating agents are presented in Chapter 10. Chapter 11 evaluates the effects of mine waste on water quality in headwater streams through the use of field studies. A good research summary on the assessment of metal contaminants dispersed in the aquatic environment of certain rivers of the People's Republic of China is presented in Chapter 12. The final chapter evaluates a purge-water-management disposal strategy to remove radionuclides and organic and inorganic chemicals from contaminated groundwater.

This book is recommended for the readers who are interested in receiving a comprehensive understanding of the biogeochemical processes related to metal contaminants in soils and groundwaters. The book is of considerable value for readers who are interested in broadening their knowledge of biogeochemical processes related to metal contaminants in soils and groundwaters. It also provides an improved appreciation of available alternative approaches for remediation of the metal-contaminated soils.

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Software for Material Safety Data Sheets

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INTRODUCTION

In today's age of cut throat competition, there is an ever increasing need to develop software packages which cater to the needs of an entire gamut of information for environmental management and control. These packages have to simultaneously fulfill the requirements of versatility and user friendliness. A software package however sophisticated will not be successful it cannot find a place among a wide variety of environmental businesses. The success of a software package can be ascertained by its utility in solving environmental problems faced by a business. More emphasis is now given on software packages which enhance the efficiency of an environmental professional for solving regulatory industrial problems [1].

Over the last 15 years the area of environmental health and safety compliance has grown considerably as a result of new environmental regulations. The area requires the use of Material Safety Data Sheets (MSDS) for various chemicals. Federal law requires all employees to have, on hand, an up-to-date Material Safety Data Sheet for every potentially hazardous material in the workplace.

This article provides a comprehensive list of the various environmental software packages available which incorporate material Safety Data Sheets. A brief overview of the software developed for MSDS by Logical Technology Inc. [Tel#: 1-800-COMPLY2, (309)-689-2911, Cost: $1250] is included for illustrative purposes [2].

AVAILABLE MSDS SOFTWARE

Material Safety Data Sheets are a primary component of safety legislation and covers the use, storage, labeling, and disposal of controlled materials. Legislation governing the MSDS requires the employees to be properly trained and knowledgeable to use hazardous products. Employers are required to obtain MSDS's for all controlled products and make them available to their employees.

This review of MSDS software is based on research from the available literature as well as relatively new source - the Internet. A list of MSDS software was prepared using three software directories published in 1995-1996:

- 1996 Guide to Environmental Software Products, Environmental Manager [3].
- 1996 CEP Software Directory [4]
- PE's Annual Guide to Environmental Software [5].

The list is provided in Table I. Information on the product including the address, telephone and facsimile number of a total of 56 suppliers, and the product name for each software is given in this table. The Internet email addresses and home page URL of the supplier is also included where available.

A NEW TREND

Recently, the Internet is becoming a rich source of information on a wide range of subjects in the technical field. The concept of Internet as an "Advisor" is what is catching on today. The Internet provides you with all the possible information and its like shopping for software packages to decide which one to buy, the main difference being that this can be done by sitting in one's office. All this decision making can be done just by browsing through the net.

It is now possible to obtain Material Safety Data Sheets on hundreds of material on the Internet. The URL's of a few of the sites which provide Material Safety Data Sheets on-line are:

- *gopher://gopher.chem.utah.edu:70/11/MSDS*

This site is maintained by The University of Utah and it supports a gopher server that contains a library of Material Safety Data Sheets on hundreds of materials. The intended purpose of this database is to provide access to students and teachers as a learning/teaching tool.

- *gopher://ecosys.drdr.virginia.edu: 70/11/library/gen/toxics*

The site is maintained by The University of Virginia and it supports a gopher server that contains a database of Chemical Substance Fact Sheets for various chemicals.

- *http://www.enviro-net.com/technical/ msds*

This site is an MSDS Archive. The Enviro-net MSDS database is a mirror of the University of Utah database and it also includes a searchable index.

- *gopher://hazard.com:3000/7*

This is a searchable Gopher index from Vermont SIRI, and uses the search function of your browser to enter search terms.

- *http://physchem.ox.ac.uk/MSDS/*

These Material Safety Data Sheets are provided by Oxford University's Physical and Chemical Theoretical Laboratory and are gathered from a variety of net and other sources.

- *http://diamond.cicsr.ubc.ca:8080/wouf /web_msds_search-t?*

These Material Safety Data Sheets are provided by the University of British Columbia.

OVERVIEW OF LOGICAL'S THE MSDS SOLUTIONS SOFTWARE

The Material Safety Data Sheet management area involves managing and handling MSDS information. The MSDS Solution software developed by Logical Technology Inc., is a menu driven system for storing, displaying, and printing MSDSs, and tracking use locations of MSDSs. The software enables querying of every field and all text to create custom reports. A comprehensive password and authorization security system limits access to entering / modifying MSDSs, creating custom reports, and assigning passwords. The software incorporates a flexible material safety tracking system, a Material Safety Data Sheet module, and Chemical Compliance Monitor into a menu driven package for comprehensive environmental tracking, including SARA 313 reporting. The MSDS solution offers an user friendly MSDS management where the users can store, display, and print MSDSs, as well as

track usage locations. MSDS management involves handling and managing of MSDS within the system: a powerful restoring function, generating reports by querying, loading / editing / copying and disposition. The various features of the Logical Software which we observed while going through the software are mentioned below.

• The MSDS Solution includes simple MSDS search procedures allowing the user to locate critical information that he needs to know. The MSDS search option allows to locate any given MSDS through different fields. The search option includes ten fields to give you different approaches to find and retrieve MSDS. MSDS search option is the heart of MSDS management area.

• A successful MSDS search leads to the options menu which provides you with four options - Display option, Print MSDS, Reference to MSDS, and SARA MSDS update. The display MSDS option provides information about the product, physical / chemical characteristics, fire and explosions, hazard data, components information and MSDS text sections. Manufacturer/Supplier validation menu allows you to enter information pertaining strictly to manufacturers and suppliers of MSDS's and provides the option to list all companies or to add/modify/and delete a company.

• Updating of existing MSDSs can be done with ease and only requires editing of potential changes. New MSDS can be loaded using the Load/Edit/Copy MSDS and the validation option. The user thus immediately gets the latest information. Validation gives control over the system pertaining to manufacturers and suppliers.

• The MSDS Solution software permits an unlimited number of sub queries. The Reports option enables to conduct MSDS queries and provides pre-determined reports. Pre-determined reports provides lists of specific MSDS's from the database, all companies within the system, shipping label, information from fire and explosion section of all current MSDS and a list of all MSDS products.

• Another feature of the software is the MSDS status system which allows MSDSs for current/approved materials to be differentiated from other MSDSs in the system. This allows the users to access all of the current MSDSs for their work areas, while still retaining the category of previously used materials. The Disposition command enables the user to disposition MSDS from one status to another status level. The status Level can be Pending, Current of Noncurrent and this is the accessibility stage.

• The option of the Function is only available to the coordinator and it provides him the tools for managing the system.

• The System Management portion of the software includes the following three options
- Access the directory
- Password Set Up
- Task Manager.
Task Manager function amplifies LOGI-CAL's emphasis on the much needed interaction between the four function levels-
- General User
- Coordinator
- Hazardous Material Professional
- MSDS Entry Personnel
Task manager is an effective tool which allows to create messages for "delivery" weeks, months, or even years in the future. Also the messages sent to the user must be answered in order for the message to "go away".

• The software also has the option to store scanned images of MSDSs. Scanned images of the MSDS can be loaded in the software thus enabling the user to view and print the MSDS exactly as it was received from the Manufacturer/Supplier.

The software also incorporates the Chemical Compliance Monitor tool which provides endless reports with compliance source lists and chemicals. Chemical Compliance Monitor is the index needed to cross reference the same chemical between various and assorted federal, state, international, and advisory bodies. The Chemical Compliance Monitor designed by Logical has compiled over 140 lists and 30000 chemical name categories. The CCM menu provides the following options - Specific chemical information, selected source lists v/s MSDS's, all source lists v/s MSDS, selected MSDS v/s source lists, all MSDS v/s source lists, chemical lists by source(s), LTI or HAZMAT glossary and source list information.
The Logical software provides a satisfactory way to manage the MSDS sheet and labeling requirements imposed by the legislation. The most updated version of an MSDS is available in workplace on workshift 24 hr./day for compliance. The MSDS Module features include - Password Security, Menu Driven with on-line Help, Standard MSDS formats, Import / Export MSDS, Entire Database reportability, Use / Customer Location Tracking, and Ease of Use. The Logical software is capable of solving MSDS organizational and compliance needs.
The software was easily installed, and found to be very user friendly. The software was tested for 15 different cases and

the output was complete from both the organizational and compliance point of view. Incorporation of the MSDS software on a CD ROM system would make it easier to install, store, access, and retrieve Material Safety Data Sheets [6]. The logical software works in a DOS environment, and, it is the WINDOWS operating system which is being used today, on almost all IBM PC's. It would make the software much more versatile if the software could be improvised to run on the WINDOWS system.

CONCLUDING REMARKS

This article takes the reader through the entire world of environmental software packages which deal with Material Safety Data Sheets. The article makes one realize the power of these software packages and the wide range that one can choose from. However more choices would mean that the environmental professional would have to judiciously choose the desired package which would serve the requirements in a most efficient and economic way.
The URL's of the sites given in this article provide the latest in the field of MSDS. Moreover the comprehensive list of commercial software available in the area of MSDS would prove to be of great help in selecting an appropriate MSDS software for your organization.

LITERATURE CITED

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2."The MSDS Solution", Logical Technology Inc., (1995).
3.Johnson, S.M., "1996 Guide to Environmental Software Products", Environmental Manager, pp 16-39, (Feb. 1996).
4."1996 CEP Software Directory", A Supplement to Chemical Engineering Progress, (Dec. 1995).
5.Hodson, C. O., A. Kilbourne, "The Limit for Software Options", Pollution Engineering, pp 53-67, (Jan., 1996).
6."CD-ROM system can assist in NAFTA Certificate of Origin Verification", Materials Performance, v. 34, pp. 41, (Sept. 1995).

Table I :

Commercial Software Available in the Area of MSDS.

Supplier	Program Name
Applied Training Resources	MSDS Maker
AV Systems Inc. 4657 Platt Road, Ann Arbor, MI 48108-9726 Tel # : (313)-973-3000: Fax # : (313)-677-4480	Material Inventory Report System MSDS + MSDS II MSDS Net View
Achieve! Technology Inc. P.O.Box 668, Amherst, NH 03031-0668 Tel# : (800)--446-3427; Fax# : (603)-595-1414 email : achieve@achieve-tech.com HomePage URL: http://www.mv.com/biz/achieve-tech/	Compliance Manager
Advanced Information Solutions, Inc. 4618 Fillingame Dr.,Suite 100, Chantilly, VA 22021 Tel# : (703)-802-9682; Fax# : (703)-802-9682	Environmental Office Management Information System Executive Information System
Alternative Systems Inc. 225 South Cabrillo Highway, Suite 124-C, Half Moon Bay, CA 94019-9924 Tel# : (415)-726-5700 ; Fax# : (415)-726-7846	TINIA
Applied Graphic Solutions Corporation P.O.Box 669, Moorpark, CA 93021 Tel# : (805)-529-5654 ; Fax# : (805)-529-7614	EnviroView
ARI Network Services, Inc. 330 East Kilbourn Ave., Milwaukee, WI 53202-6636 Tel# : (414)-278-7676 ; Fax# : (414)-283-4357 email : grzelak@arinet.com HomePage URL: http://www.arinet.com/	Custom Comply (Agriculture & Specialty Chemicals)
Automated Compliance Systems 245 Highway 22 West, BridgeWater, NJ 08807 Tel# : (908)-707-4100 ; Fax# : (908)-707-1179 email: marketing@acssoft.com HomePage URL: http://www.acssoft.com/	Seedpak LIMS Total Compliance Framework (TCF)
BC Hydro and Power Authority 6911 Southpoint Drive, E-07, Burnaby, BC V3N 4X8, CANADA Tel# : (604)-528-3316 ; Fax# : (604)-528-3347 email: Bill.Fernihough@bchydro.bc.ca HomePageURL: http://www.bchydro.bc.ca/	MSDS Squared MSDS Squared
Byte Rite, Inc. P.O.Box 422-Planetarium Station, New York, NY 10024-0422 Tel# : (212)-496-6188 ; Fax# : (212)-721-6754	MSDS-Rite TrackRite

CamAxys 8 The Meadow, Meadow Lane, St. Ives, Cambridge PE 17 4LG, UNITED KINGDOM Tel# : +44-1480-497739 ; Fax# : +44-1480-497759	CamHealth for COSHH CamHealth for Material Safety data CamHealth for the Environment
Canadian Center for Occupational Health	CCINFO Disc, Series A1-MSDS CCINFO Disc, Series A3 - FTSS
Chemical Abstracts Service-STN International 2540 Olentangy River Road, P.O.Box 3012, Columbus, OH 43210-0012 Tel# : (800)-753-4227 ; Fax# : (614)-447-3713 email: help@cas.org HomePage URL: http://www.cas.org/	MSDS-CCOHS Database STN Express
Chemical Information Systems, Inc. 810 Gleneagles Court, Suite 300, Towson, MD,21286 Tel# : (800)-247-8737, (410)-321-8440 Fax# : (410)-296-0712	BAKER/MALLIN MSDS Databases
Chemical Safety Corp. 1301 South 46th Street, RFS 180-11, Richmond, CA 94804-4603 email: chemsafe@ix..netcom.com HomePage URL: http://www.portal.com/~austin/chemsafe/	EMS Ad Hoc Management Reports EMS Chemical Inventory/MSDS Access System EMS Material Safety Data Sheet (MSDS) Management Environmental Management System
CHEMTOX, Div. of Resource Consultants Inc. 7121 CrossRoads Boulevard, P.O. Box 1848 Brentwood, TN 37024-1848 Tel# (800)-338-2815 , (615)-373-5040 Fax# : (615)-370-4339	Inventory Management Label System MSDS Author MSDS Management SARA Title III Reporting Module
ChemAdvisor	ChemSDS+ LOLI
Corbus Inc.	Lab Trail MSDS Basic MSDS Scan Terms Windows
Crossfields Inc. 633 North 9th Street, P.O.Box 311, Santa Paula, CA 93061-9975 Tel# : (805)-933-1385 ; Fax# : (805)-933-3397	Haz : Base
Datastream Systems	MP2 for Windows
Datacor	Imagepax Labelpax
Decision Dynamics	eMSDS
Delta Systems Inc.	MSDS - Stars
Dolphin Software, Inc. 9 Monroe Parkway, Suite 150, Lake Oswego, OR 97035 Tel# : (800)-275-MSDS ; (503)-635-6455 Fax# : (503)-635-5626	Comply Plus

EcoSystems Inc.	ChemBase ChemBasic
EnviroMetrics Software Inc. 92 Read's Way, New Castle, DE 19720 Tel# : (800)-355-9136 ; (302)-324-9136 Fax# : (302)-324-9138 email: sales@enviro.com	PlantWare/Chemical Physical Properties PlantWare/Hazardous Waste Manifests PlantWare/MSDS and Chemical Inventory PlantWare/ Waste Tracking
EnviroWin Software Inc. 2032 West Cullom Av.,Suite One, Chicago, IL 60618-1702 Tel# : (800)-454-0404 ; (312)-244-1900 Fax# : (312)-244-1922	MSDS Finder Material Safety Data Sheets on CD-ROM MSDS Report Manager Templates eMSDS Electronic
Foster Wheeler Environmental Corp. Genium Publishing One Genium Plaza, Schenectada, NY 12304-4690 Tel# : (800)--243-6486 ; (518)-377-1891 email: info@genium.com HomePage URL : http://www.chemweek.com/genium/	MSDS Module MSDS Collection on CD-ROM MSDS Collection on CD-ROM / Chemical Week Buyer's Guide MSDS Form Template Software
GRC International Inc. 1900 Gallows Road, Vienna, VA 22182-3865 Tel# : (800)-934-5917 ; (703)-506-5166 Fax# : (703)-760-8747 email: flow-gemini@grci.com HomePage URL: http://www.grci.com/	Flow Gemini
Haxmat America, Inc. 9 Browning Road, Arlington, MA 02174 7011 Tel# : (617)-6346-4564 ; Fax# : (617)-646-4564	1993 U.S. DOT Emergency Response Guidebook Bretherick's Reactive Chemical Hazards Database Electronic NIOSH Pocket Guide to Chemical Hazards
Hazmat Control System 5199 East Pacific Coast Highway, Suite 500, Long Beach, CA 90804-3307. Tel# : (310)-597-7995 ; Fax# : (310)-597-9904 email: hazmat@ix.netcom.com	CiDATA HazKNOW " Know-It-All" MSDSFILE
HazWaste Tcchnologies Corporation 2995 Center Green Court South, Boulder, CO 80301-5421 Tel# : (800)-492-7832 ; (303)-440-5664 Fax# : (303)-440-5731	HazInfo: MSDS
Hazox Corp.	Environmental Management System
Heart Information Systems Instant Reference Sources, Inc. 7605 Rockpoint Drive, Austin, TX 78731 Tel# : (800)-301-0359 ; Fax# : (512)-345-2386	The WERCS Instant EPA's Air Toxics Instant EPA's IRIS Instant EPA's Pesticide Facts Instant Gloves + CPC Database
Jordan Systems	Hazardous Materials Manager
Khem Products Inc. 1217 Bush Road, P.O.Box 161, Abingdon, MD 21009 Tel# : (410)-679-6620 ; Fax# : (410)-679-6625 email : info@khem.com, sales@khem.com HomePage URL: http://www.khem.com/khem/home.html	Khem Safety

Knorr Associates 10 Park Place, P.O. Box 218, Butler, NJ 07405-0218 Tel# : (201)-492-8500 ; Fax# : (201)-492-0453 email: mailroom@knorr.com HomePage URL : http://www.knorr.com/	DataPipe
Logical Technology 5113 North Executive Drive, Peoria, IL 61614-4868 Tel#:(800)-COMPLY2, (309)-689-2911 email: logical@comply1.com	Hazmin LogiTrac The MSDS Solution
Marcom Group, Ltd. 20 Marcom Parkway, Boothwyn, PA 19061 Tel# : (800)-654-CHIT, (610)-859-8106 Fax# : (610)-859-8106	CD-ROM Training - Right-to-Know Chemical Hazard Identification & Training Computer-Based Training- Right-to-Know/MSDS
Micromedex	Chemmate
Modern Technologies Corporation 4032 Linden Avenue, Dayton, OH 45432-3015 Tel# : (513)-252-9199 ; Fax# : (714)-252-9227	InforM Safety Data System LINDEN Environmental Management System
MSDS Network	MSDS Standard
North American Software P.O.Box 1197, Lake Forest, CA 92630 Tel# : (800)-966-5678, (714)-457-9937 Fax# : (714)-457-9941	HAZARD Waste Label Printing System MSDS-UC DOS MSDS-UC Windows
Optimal Care, Inc. 4222 East Camelback Road, Suite H 220 Phoenix, AZ 85018 Tel# : (800)-968-4664 , (602)-264-8000 Fax# : (602)-952-0866 email: 75404.1661@compuserve.com	Sentry 2000
Oracle Energy Global Business Center Two Allen Center, 1200 Smith Street, Suite 2700 Houston, TX 77002 Tel# : (800)-968-4664, (713)-750-5052 Fax# : (713)-654-8743	Oracle Environmental
PARS Environmental Services 6 South Gold Drive, Suite A, Robbinsville, NJ 08691 Tel# : (800)-959-1119, (609)-890-7277 Fax# : (609)-890-9116	MSDS Monitor
Prime Systems, Inc. 32915 Aurora Road, Suite 100, Solon, OH 44139 Tel# : (216)-248-3322 ; Fax# : (216)-248-7202	Prime Time ECS Prime Time PM for Windows
Quantum Software Solutions	Facility Tracking System Waste Information Management System

Radian Corp. 8501 Mo-Pac Boulevard, P.O. Box 201088 Austin, TX 78720 - 1088 Tel# : (800)-654-4281, (512)-454-4797 Fax# : (512)-454-8807 email: clint_waggoner@ccmail.radian.com HomePage URL : http://www.radian.com/	R-EDMS
Siemens Nixdorf Information Systems AG ASW GIS / ENV, Otto-Hahn-Ring 6, D-81739, Munchen, GERMANY Tel# : +49-89-636-41988, Fax# : +49-89-636-45202 HomePage URL: http://www.sni.de/	IGS (Information System on Hazardous Substances)
Solutions Software 1795 Turtle Hill Road, Enterprise, Fl 32725 Tel# : (407)-321-7912 ; Fax# : (407)-323-4898 email: solution@iag.net HomePage URL:http://www.gate.net/solutions/	Chemical Compatibility Database TSCA Chemical Data on CD-ROM
Technical Database Services Inc.	AQUIRE Chemical Compliance Monitor DIPPR 10.2 ECDIN EFD Numerica Online PPDS 2 SYNDEX
Telecation Inc. 7112 West Jefferson Avenue, Suite 307, Lakewood, C0 80235 Tel# : (303)-987-0980 ; Fax# : (303)-987-0984	Chemical Inventory Log
Telestar 750 Warm Springs Ave., Boise, ID 83712-6457 Tel# : (800)-441-3894 , (208)-343-3894 Fax# : (208)-385-9168	HazE HazeETraining
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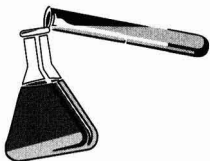
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Design for Pollution Control: Screening Alternative Technologies

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Identifying potential solutions to complex problems using a minimum of information is important in a wide range of circumstances. Tools for this purpose are key to sound decisions and require careful thought and implementation. This article describes the development and use of a screening tool to allow a utility, Houston Lighting & Power Company, to provide technical support to its process industry customers. The objective is to provide advice to these companies regarding cost and energy efficient technologies which can address this industry's environmental and other processing problems.

INTRODUCTION

The design of industrial processes is iterative, no matter what the job or the desired outcome. Design begins with general objectives and a rough initial concept and then proceeds through many levels of definition until a final, detailed and implementable version has been produced.

The early stages of design may be more for the purposes of planning and screening of alternatives than for actual implementation. These early evaluations are very important, however, because they establish the path down which the more detailed work will eventually proceed.

There are seemingly unreconcilable demands on these early design activities. They must be carried out quickly and with limited information, yet they must be reliable enough to screen out unattractive alternatives and to retain the promising ones.

Much has been written about using a structured approach for design [1, 2]. From this work emerges some very useful guiding principles. First, it is important to understand processes as integrated systems using fundamental principles. Thermal pinch analysis and mass pinch analysis combined with process modeling are recommended for this purpose [2]. Another important concept is how the design job is decomposed successively into smaller, more tractable design tasks and then how these smaller tasks are resolved. The method of decomposition, the questions addressed at each level and the calculations made are all important [1].

As design proceeds from the general to the specific, the design engineers must be able to proceed smoothly in their work from one level of detail to the next. Models and data developed for screening should be extendable to the more detailed work. This means that it is important not only to have an overall work strategy, but also to have design tools that support the strategy.

In this paper, we address this issue and discuss how design for pollution control can proceed from the earliest levels of screening to the more detailed levels of design and implementation. This will be illustrated using a specific screening tool developed to allow a utility, Houston Lighting & Power Company, to provide technical support to its industrial customers regarding the use of "electrotechnologies" within these customers' production facilities. See Table 1 for a listing of technologies considered.

BUSINESS NEED

Design begins with planning, setting objectives and screening alternatives. These activities might be performed by many different people and organizations with different information needs and perspectives on the final outcome.

Within a company, the environmental manager might wish to understand the impact of new environmental regulations on the company's production facilities. What is the magnitude of the problem, do feasible alternatives exist, and what are their costs and performances? This information is used to advise management, to plan, and to set budgets.

A consulting company might be asked to assess a customer's situation and identify alternative strategies: for debottlenecking, for meeting environmental regulations, or for changing to a different feedstock. This consultant's responsiveness and quality of advice are important both to the company retaining these services and to the consultant whose reputation and future business prospects depend upon giving sound advice.

Or, a utility may wish to provide a broader electricity service to its industrial customers. In addition to competitively priced and reliable power, the utility might wish to provide technical information and support relating to tech-

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9. Pressure Swing Adsorption (PSA)	23. Motors/Variable Speed Motors
10. Ozonation	24. Process Cooling (Chilling, Refrigeration)
11. Stripping	25. Molten Metal Technology
12. Crystallization	26. Electrolysis
13. Electrostatic Precipitation	27. Incineration
14. Baghouse Filters	

nologies that can address their customers' production problems. It is this example that we shall develop in more detail.

Specific Requirements

Houston Lighting & Power Company (HL&P) has adopted a strategy of enhancing the health and competitiveness of their petrochemical industry customers [3].'

The objective is to foster the use of effective electrotechnologies to address this industry's urgent processing, environmental and energy needs. Companies must expand capacity, meet product quality requirements, comply with environmental regulations, and rationalize site heat and power systems to accommodate changing production demands. All of these require the use of electrotechnologies.

Providing the services planned by HL&P requires a thorough understanding of the petrochemical industry's needs. What market forces are these companies facing, what specific processing and energy needs do they have, what technologies can address these needs, what are the barriers to the use of these technologies, and what infrastructure must be in place to promote the use of these technologies?

To answer these and other questions, HL&P retained Matrix 2000 to undertake a petrochemical industry needs assessment. Part of this work involved identifying and screening technologies that solve this industry's environmental and other processing problems.

A screening tool was needed for this purpose which would meet the following requirements:

- It could be used by Matrix 2000 or by HL&P's staff to identify technologies which address specific customer problems.
- It would provide general technical information about these technologies including: description, typical applications, performance, limitations, environmental impact, benefits, competing technologies, and approximate capital and operating costs.
- Models could be run for individual customer problems to provide specific cost and performance information.
- Material could be printed describing the technology and a simple flowsheet could be generated and

printed showing the technology's application and performance.

IMPLEMENTATION

Screening of alternatives requires a judicious tradeoff among conflicting considerations.

The results must be accurate enough to separate the attractive from the unattractive. And they must be generated quickly to conform with tight planning schedules. The user requires reasonable assurance that a potential winner is not rejected and that those retained are valid candidates and are worth the effort of further consideration.

At the same time, information and data upon which to make these judgements are usually unavailable when screening is performed. Further, those performing the assessments are often generalists and not technical specialists in each candidate technology. The screening tool must strike the proper balance.

Example: VOC Removal via Condensation

The approach used to strike this balance will now be illustrated through an example. Volatile organic compounds (VOCs) can be removed from vent streams using a number of technologies such as absorption, adsorption, condensation/refrigeration, corona discharge or incineration. Each of these is a potential candidate and should be considered during screening.

Limited data are available at the time of screening and the challenge is to understand as much as possible about the application of a technology using only this limited information. The simplified models developed and used for this purpose should be consistent with the fundamental phenomena governing the performance of these technologies. This provides confidence that the models have the right form and it allows for easier migration from simple to more complex models.

In developing the approach we, therefore, started with full descriptions of each technology and the governing rigorous heat and material balance equations. These were then systematically simplified to produce models for which data could reasonably be produced during screening. The results of the simplified models were then tested against the more rigorous ones to assure acceptable agreement. For the
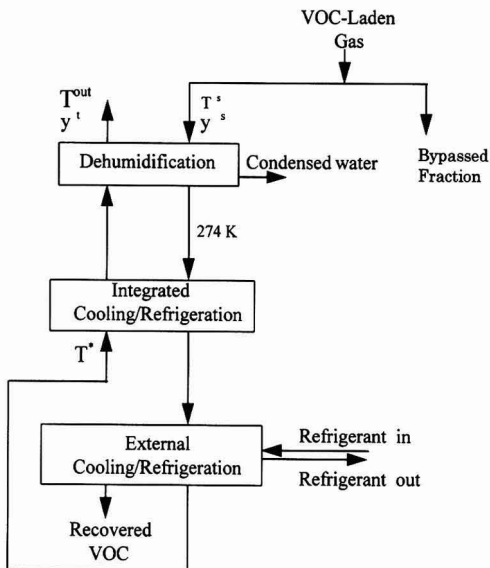
FIGURE 1 Schematic representation of the VOC-recovery system.

FIGURE 2 Pinch diagram for the VOC-condensation system.

bulk of the technologies, the agreement was within ±50% for their targeted range of application. This is the typical accuracy of cost estimates at the screening stage.

The removal of VOCs via condensation can be accomplished using the approach shown in Figure 1. Here a VOC-laden gas stream is split into a fraction to be processed and a fraction to be bypassed. The stream to be processed is dehumidified, cooled through heat integration with itself, and then cooled using a refrigerant. The gas stream, less the condensed VOC, is then heated through heat exchange before being discharged.

Richburg and El-Halwagi [4] have solved the problem of finding the least cost application of this technology to any VOC-laden gas stream given a range of refrigerants from which to choose.

The optimum solution is a tradeoff between operating cost and capital cost. The operating cost is determined by the minimum amount of the least cost refrigerant that will condense the VOC. The capital cost is determined by the fraction of the original stream that is processed and by the driving forces selected for the three heat exchangers.

In performing these calculations, it is necessary to generate the cooling curve for the VOC-laden gas stream to determine the minimum amount of refrigerant required to condense the VOC. This is used as shown in Figure 2. Here it is assumed that heat recovery occurs between the exhaust stream and the incoming VOC-laden gas. See Figure 1.

Solving the problem rigorously requires thermodynamic data from which the VLE and thermal characteristics of the system can be calculated. This is not feasible at the screening level.

Simplifying assumptions can transform the model into one which requires knowing only the gas flow rate. This model, however, still contains the important features of the technology's performance. The assumptions are:

- The gas stream is air.
- All of the VOC-laden stream is processed, none is bypassed.
- The VOC concentration is low such that the latent heat effects are small compared with sensible heat. This means that the heat capacities are constant and the cooling curves are straight lines.
- The driving forces for all heat exchangers are set at "experience" levels of 20°C.
- The refrigerant is liquid nitrogen which is available from storage tanks on site. The temperature of this refrigerant is low enough to reduce the VOC concentration to the required level.
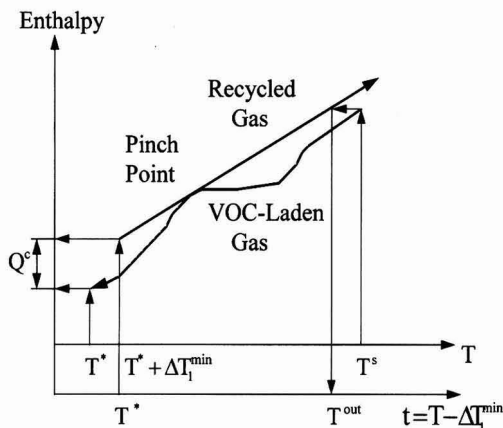
With these assumptions, the rigorous model reduces to the following simplified form (where G is the gas flow rate): (See reference [4] for the details.)

Operating Cost

$$\frac{\$}{yr} = 5.12 * G\left(\frac{ft^3}{min}\right)$$

Cost includes purchase and storage of liquid nitrogen. Operation is 8000 hrs/yr.

Power and Electricity Requirement

$$kVA = 0.011 * G\left(\frac{ft^3}{min}\right)$$

$$\frac{kWhr}{yr} = 89 * G\left(\frac{ft^3}{min}\right)$$

Total Capital Cost

$$\$ = \$81 * \left[(25G)^{0.6} + (83G)^{0.6} + (10G)^{0.6}\right] + \$725,000$$

Cost includes 3 heat exchangers, liquid nitrogen storage tank, installation, electrical, engineering, piping, etc.

As can be seen, the capital cost equation reflects the fact that three exchangers are included in the design.

APPLICATION

This approach was used to develop screening level models for over 20 technologies with potential application to the process industry (See Table 1). The models and the accompanying technical information about the technologies are programmed to run on a PC under Microsoft Windows.

Detailed interviews were conducted face-to-face with 35 of HL&P's petrochemical industry customers to identify their specific priorities and investment projects. Approximately 150 such projects were identified which fell into ten different categories. Six of these were environmental and four were production and infrastructure related.

It is clear that reducing pollution to meet environmental regulations is a major concern to these companies and was the single topic most on the minds of those interviewed.

The screening tool was used to assess the application of the 20 plus technologies to the approximately 150 investment projects identified. The objective was to determine their suitability, the probability they would be selected over competing technologies, and the economic and environmental impact of using the technologies.

It was found that these electrotechnologies have an enormous beneficial impact on emissions. Pollutants can be removed from air and water streams and hazardous waste can be destroyed using many different technologies. Most of these have the added feature of capturing and recycling the pollutants, creating a positive return on the investment.

This environmental cleanup can be done with modest amounts of electricity. Electricity use, therefore, offers industry an effective and inexpensive way to address one of their critical needs.

SUMMARY AND CONCLUSIONS

Judiciously designed and applied models have been shown to be very valuable for screening alternative technologies for solving environmental problems. They can be applied quickly and they can discriminate between those technologies that should be considered further and those that should be discarded.

A screening tool has been developed and programmed for this purpose. It can be used by different individuals and organizations for a wide range of technology screening objectives.

Following screening, it is necessary to perform more detailed engineering assessments using more rigorous models. Because of the manner in which the screening models were developed, they are compatible in form with the rigorous models making migration between levels of detail more straightforward.

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Stripping of VOC's From Dissolved Air Flotation

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A pilot scale study was performed to assess gas phase emissions of volatile organic compounds (VOCs) from the dissolved air flotation process. A high degree of mass closure was observed in experiments using tapwater dosed with a cocktail of VOCs, indicating that techniques employed to characterize the pilot plant were valid. Subsequent dosed wastewater experiments examined volatilization from a wastewater matrix that contained oils and suspended solids as well as investigating the impacts of hydraulic loading and recycle rate on the fate of the VOCs in the dissolved air flotation unit. Emissions of the dosed candidate compounds, calculated as a percentage of the influent mass flow, ranged from 0.2% of 1,1,2,2-tetrachloroethane to 9.9% of tetrachloroethylene. Hydraulic loading and compound type had a statistically significant effect on the emissions of VOCs, however, a high degree of interaction between parameters was observed. Effluent recycle had a greater effect on emissions at the higher hydraulic loading than at the lower loading. A model which incorporated stripping by bubbles, volatilization from a quiescent oil-free surface and equilibrium partitioning to oil was developed. The model was able to simulate the candidate compound response under all experimental conditions except the case with low hydraulic loading and low recycle rate. The results suggest that the surface volatilization model may underestimate emissions. It is hypothesized that the presence of a float in the form of a foamy layer with a high surface area tends to increase liquid-gas mass transfer of the candidate compounds over that assumed in the surface volatilization model.

INTRODUCTION

The transfer of volatile organic compounds (VOCs) from wastewater to the atmosphere during wastewater treatment has become an issue of concern in recent years. The chemicals which have been identified in offgases from wastewater processes include toxic air contaminants (TACs), ground level ozone generators and stratospheric ozone depletors. In the U.S., national emissions standards for hazardous air pollutants (NESHAP) have been established under the Clean Air Act Amendments (CAAA) of 1990. The hazardous organic NESHAP (HON), which was developed primarily for the synthetic organic chemical manufacturing industry (SOCMI), identifies wastewater collection and treatment as an area of potential air emissions.

Dissolved air flotation (DAF) is a wastewater treatment process that separates suspended solids and colloidal matter from wastewater streams. In dissolved air flotation a waste stream is pressurized to dissolve excess air, and subsequently depressurized to release the air from solution. When the pressure is reduced, the air forms bubbles around wastewater particles which act as nucleoids, and as the bubbles rise to the water surface, the particles are drawn along with them. As the particles accumulate at the surface, a scum or separate oily phase will form which is then skimmed off of the flotation tank surface for subsequent disposal. VOCs may be emitted by the release of contaminated bubbles from the flotation tank, volatilization from the float on the surface of the flotation tank, and volatilization from the exposed water on the surface of the flotation tank. Gas phase emissions from the DAF process may be significant when located near the head end of a waste treatment train where high concentrations of VOCs are present in the wastewater stream. The petroleum refining industry typically employs dissolved air flotation in this manner.

The contribution of the previously defined mechanisms to the overall volatilization in the process will depend upon the fractional saturation of the bubbles, the partitioning of the VOCs to the oil phase and the impact of the presence of the float on the volatilization of VOCs from the flotation tank surface.

The objectives of this study were therefore to:

- measure the emissions of VOCs from a pilot scale dissolved air flotation unit
- assess the impact of hydraulic loading and recycle (and hence air to liquid ratio) on the liquid-gas mass transfer of VOCs from dissolved air flotation units
- develop and verify models for VOC emissions from dissolved air flotation units.

MODEL DEVELOPMENT

In the model development, stripping by bubbles, surface volatilization and partitioning to oil were considered as re-

moval mechanisms. Bubbles generated in the flotation basin of a DAF process are formed at the microscopic level and increase in size with agglomeration and pressure reduction as they rise to the surface of the basin [1]. The bubbles have a very high surface to volume ratio that enhances liquid-gas mass transfer. Hence, for the purposes of modeling it is assumed that the gas phase concentration of a VOC, upon exiting the liquid surface of the flotation tank, is in equilibrium with respect to the liquid phase concentration. The rate of stripping to the bubbles will therefore equal:

$$r_s = Q_g C_l H_c \qquad (1)$$

where:

r_s = rate of stripping, mg/hr
Q_g = flow rate of air bubbles exiting liquid surface, m³/hr
C_l = liquid concentration of VOC in the flotation basin, mg/m³
H_c = Henry's law coefficient, m³ liquid/m³ gas

The product $C_l H_c$ is the concentration of the VOC in the bubbles exiting the liquid and this concentration is greater than the VOC concentration of the gas layer above the liquid. The offgas flow rate (Q_g) can be estimated from the recycle flow rate, pressure and temperature [1].

In the model, the rate of volatilization from the surface of the flotation basin is defined as:

$$r_v = K_L A \left(C_l - \frac{C_g}{H_c} \right) \qquad (2)$$

where:

r_v = rate of volatilization, mg/hr
K_L = liquid-gas mass transfer coefficient, m/hr
A = tank surface area, m²
C_g = gas phase concentration above liquid surface, mg/m³

The mass transfer coefficient (K_L) is defined as:

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_g H_c} \qquad (3)$$

where:

k_l = liquid phase mass transfer coefficient, m/hr
k_g = gas phase mass transfer coefficient, m/hr

The mass transfer coefficients for surface volatilization are estimated using the correlations developed by Mackay and Yeun [2]. The gas phase mass transfer coefficient is calculated as:

$$k_g = \left(1 \times 10^{-3} + 46.2 \times 10^{-3} U^* Sc_G^{-0.67} \right) \times 3600 \qquad (4)$$

The liquid phase mass transfer coefficient is calculated as either:

$$k_l = \left(1 \times 10^{-6} + 34.1 \times 10^{-4} U^* Sc_L^{-0.5} \right) \times 3600 \ (U^* > 0.3) \qquad (5)$$

or:

$$k_l = \left(1 \times 10^{-6} + 144 \times 10^{-4} U^{*2.2} Sc_L^{-0.5} \right) \times 3600 (U^* < 0.3) \qquad (6)$$

where:

$U^* = 10^{-2}(6.1 + 0.63U_{10})^{0.5} U_{10}$
U^* = air side friction velocity, m/s
U_{10} = wind velocity 10 m above the water surface, m/s
Sc_G = gas phase Schmidt number, dimensionless
Sc_L = liquid phase Schmidt number, dimensionless.

This derivation assumes that volatilization from the surface of the DAF is the same as volatilization from clean water. Under normal operation DAF surfaces are usually partly covered with oil, and for completeness, mass transfer from the oil covered surface should be addressed separately. However, the fraction of the surface area which is covered with oil usually varies temporally, depending upon the mechanism of float removal. Mass transfer through an oil film will likely be less than that through an equivalent water film due to increased viscosity, reduced diffusivities and enhanced solubilities of the contaminants in the oil. Because of the uncertainties associated with the fraction of the surface that is covered with float, the proposed model only addresses volatilization from an open water surface, as this should provide a maximum estimate of emissions.

The model assumes that partitioning of VOCs to oils can be modeled by a compound's octanol-water partitioning coefficient (K_{ow}). Barbari and King [3] have demonstrated that the partitioning of VOCs to octanol is similar to partitioning to oils. Therefore, the partitioning is modeled as:

$$q = \frac{K_{ow}}{\rho} C_l \qquad (7)$$

where:

q = mass of contaminant sorbed per mass of oil, μg VOC/mg oil
ρ = density of octanol, mg/L

In the following mass balance equations the term K_{ow}/ρ will be referred to as K_p. The mass balance equation for the liquid phase of the flotation basin was based on an assumption of a completely mixed flow regime and was therefore defined as:

$$Q_0(1 + K_p O_0) C_0 - Q_1(1 + K_p O_1) C_1 - Q_2(1 + K_p O_2) C_1$$
$$- Q_g H_c C_1 - K_L A \left(C_1 - \frac{C_g}{H_c} \right) = 0 \qquad (8)$$

where:

O_0, O_1, O_2 = oil concentrations in the influent, effluent and float respectively, g/m³
C_0, C_1 = contaminant concentrations in the influent and effluent respectively, mg/m³
Q_0, Q_1, Q_2 = flow of the influent, effluent and float respectively, m³/hr
$Q_1 = Q_0 - Q_2$

Since the DAF under study was covered and vented, a mass balance was also performed on the headspace. The mass balance assumes that the influent sweep air is free of the VOCs and the resulting equation for the gas phase was defined as follows:

$$- Q_{sweep} C_g + Q_g H_c C_1 + K_L A \left(C_1 - \frac{C_g}{H_c} \right) = 0 \qquad (9)$$

where:

Q_{sweep} = flow rate of sweep air through headspace, m³/hr
Equations 5 and 6 were solved simultaneously to determine the fate of the VOCs in the DAF.

MATERIALS AND METHODS

Wastewater Source

The study was conducted at an oil refinery in southwestern Ontario. The refinery is designed to process approximately 90,000 barrels per day of Western Canada crude to produce gasoline, diesel oil, jet fuel, heating oil and bunker oil. The wastewater stream from the refinery has a flow of approximately 6500 m³/d and is neutralized with caustic soda to a pH ranging from 9.5 to 9.7. Prior to DAF treatment the wastewater is conditioned with polymer and allowed to flocculate for a period of 6 to 8 hours. The wastewater employed for this study was pumped directly from the flocculation tanks and therefore did not require further treatment prior to the pilot DAF system.

Dissolved Air Flotation Pilot Plant

The DAF pilot plant was rented for the purposes of the study and has been employed by the manufacturer in numerous prior feasibility tests. A flowsheet describing the DAF process is presented in Figure 1. The wastewater stream entered directly into the flotation tank which had a volume of 1.9 m³ and a surface area of 1.25 m². A recycle stream was withdrawn from the bottom of the flotation tank and pumped into a pressurization tank. A solenoid controlled valve regulated the air pressure in the tank in the range of 63 to 65 psig. The air pressure was employed to push the recycle stream through a flow controlling valve and into the flotation tank. The wastewater flow rate was set and monitored using a calibrated barrel and a stopwatch.

The headspace of the DAF tank was essentially sealed from the atmosphere using galvanized steel sheeting. The headspace volume was estimated to be 0.5 m³. The DAF tank normally employs a continuous scraper which removes the float from the flotation tank surface. However, the presence of the cover interfered with operation of the scraper, and therefore, the scrapers were not employed in this study. For the purposes of this study the float was manually removed from the flotation tank surface as re-

quired. A vacuum cleaner was employed to withdraw air from the headspace with makeup air pulled from the surrounding ambient air through narrow gaps in the headspace cover. A flow controlling valve and an inline rotameter were employed to fix the venting rate. The induced flow rate was greater than that of the released bubbles, and therefore, the emissions observed in these experiments would likely be greater than those observed in covered, non-ventilated DAFs. The emissions may however, be less than those observed for non-covered DAFs.

In all of the experiments conducted in this study, the influent was dosed with a methanol solution which contained the candidate compounds (Table 1). During dosing, this solution was pumped with a peristaltic pump from a Tedlar™ storage bag into the waste stream through a fine orifice located upstream of the pilot plant. Samples of the dosing solution were collected at intervals during the experimental regime. Analysis of these samples revealed measured concentrations that were consistent over time and in agreement with the target concentrations. It was therefore apparent that the candidate compounds had completely dissolved in the methanol and there were minimal losses of the candidate compounds through the bag wall. The dosed wastewater stream passed through a 5.1 cm diameter stainless steel, helical, in-line mixer prior to entering the flotation tank to ensure that the target compounds were thoroughly dissolved in the wastewater prior to entering the flotation tank.

Experimental Plan

The experiments conducted in this study consisted of three dosed tapwater experiments and eight dosed wastewater experiments. Dosed tapwater experiments were performed to assess the validity of the dosing and sampling procedures and to provide a baseline reference of the behaviour of the candidate compounds in the absence of an oily phase. Three steady-state dosed tapwater experiments were performed to assess experimental replicability. In all experiments, steady state was defined after the flotation basin headspace had been allowed to turn over 3 times, once the flotation basin contents had already been allowed to turn over 3 times. In the dosed tapwater experiments, the pilot plant was operated with an influent flow rate of 4.54 m³/hr, a recycle flow rate of 4.54 m³/hr, a recycle pressure of 63 psig and a liquid temperature of 23°C.

The dosed wastewater experiments examined the volatilization from a wastewater matrix that contained oils and suspended solids as well as investigating the impacts of hydraulic loading and recycle rate on the fate of the VOCs in the dissolved air flotation unit. A 2² factorial design with complete replication of factors was employed and the experimental conditions for the dosed wastewater experiments are summarized, along with the experimental order, in Table 2. The temperature of the pilot plant contents ranged from 29.5 to 33°C over the experimental period. A headspace sweep air flow rate of 8.5 m³/hr was maintained in each experiment.

Sampling and Analysis

Conventional parameters were monitored to ensure that the pilot plant was operating under conditions that are representative of full scale processes and included pH, influ-
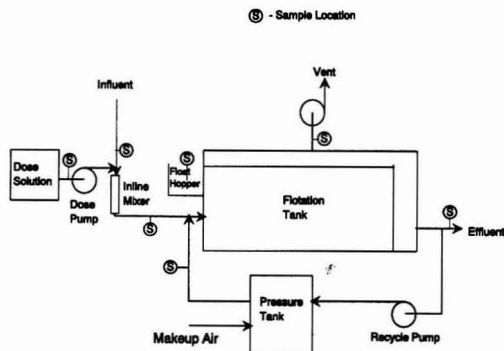
FIGURE 1   Pilot DAF flow schematic

TABLE 1. Properties of Model Compounds

Compound	EPA Priority Pollutant List	EPA 40 POTW Study[1] (% detect)	Henry's Law Coefficient m^3 liq/m^3 gas	Log K_{ow} Partition Coefficient
Chloroform	Y	91	0.150[5]	1.97[2]
1,1,1-Trichloroethane	Y	85	0.703[5]	2.47[2]
Trichloroethylene	Y	90	0.392[5]	2.53[2]
Toluene	Y	96	0.277[4]	2.69[2]
Tetrachloroethylene	Y	95	0.723[5]	2.53[2]
o-Xylene	N	NA	0.210[4]	3.12[3]
Bromoform	Y	2	0.018[6]	2.30[2]
1,1,2,2-Tetrachloroethane	Y	7	0.011[4]	2.56[2]
1,3,5-Trimethylbenzene	N	NA	0.290[4]	3.42[2]
1,4-Dichlorobenzene	Y	17	0.137[4]	3.39[2]

Note: All Henry's Law coefficients at 25°C.
NA—Not Available.
[1] Burns and Roe (1982) [4].
[2] USEPA WERL Database (1990) [5].
[3] Howard (1990) [6].
[4] Ashworth et al. (1988) [7].
[5] Gosset (1987) [8].
[6] Munz and Roberts (1989) [9].

ent, effluent and float suspended solids (total and volatile) and oil and grease concentrations. Samples for suspended solids and oil and grease were collected in glass jars and analyzed in the laboratory. Suspended solids analyses were performed as per Standard Methods [10]. The oil and grease analysis was the Partition-Gravimetric method described in Standard Methods [10].

In each experiment, liquid phase samples were collected at steady state for VOC analysis from the non-dosed wastewater, dosed influent, flotation tank effluent and float streams. The liquid samples were coincidentally collected in two 40 mL vials which, prior to sampling, had been dosed with 0.5 mL of preservative solution that contained 80 g/L of $CuSO_4$. Preservative was added to inhibit bacterial action between the time of sampling and analysis. Where possible, the samples were collected directly from a sampling port and, if necessary, samples were initially collected in a glass beaker prior to pouring into the vials.

Gas phase samples for VOC analysis were collected from the headspace sweep air after steady state had been achieved in every experiment along with occasional (one sample on 3 separate days) sampling of the ambient air. The gas samples were collected as grab samples in 6 L passivated stainless steel, evacuated canisters. The sweep air samples were collected from a manifold which was installed in the flotation chamber headspace.

Liquid samples were analyzed for VOCs with a Tekmar model LSC 2000 concentrator equipped with a Tekmar 2016 autosampler coupled to a Hewlett-Packard 5890 gas chromatograph (GC). The GC was interfaced to a Hewlett-Packard model 5970B mass selective detector (MSD). The gas chromatographic column was a 30 m long DB-624 with an internal diameter of 0.32 mm. The isotope dilution technique (USEPA Method 1624) was employed to correct for losses through the analytical procedure. Gas samples were analyzed using a cryogenic gas sample concentrator joined to an HP 5890 GC with an HP model 5970 MSD. The chromatographic column was a DB1 with a length of 60 m and an inside diameter of 0.32 mm.

RESULTS AND DISCUSSION

Dosed Tapwater Experiments

Three replicate experiments were performed with tapwater that was dosed with the candidate compounds. Consistent behaviour was observed in the replicate experiments, and hence, Table 3 presents, as an example, the concentrations measured in the third experiment. With the exception of chloroform, negligible quantities of the candidate compounds were present in the non-dosed tapwater. Chloroform was constantly present in the non-dosed tapwater with an approximate concentration of 20 μg/L. Since all of the compounds were present at either negligible or constant values it is believed that fluctuations in the background concentrations did not substantially influence the conclusions arrived at in these experiments.

It is apparent from Table 3 that a high degree of replication between duplicate samples was attained, thereby indicating consistency in the sampling and analytical techniques employed. Table 3 also indicates only slight differ-

TABLE 2. Summary of Process Conditions for Experiments Conducted with Wastewater

Experimental Order	Liquid Flow Rate (m^3/hr)	Recycle Flow Rate (m^3/hr)	Recycle Ratio (%)
1	2.27	2.27	100
2	2.27	1.14	50
3	4.54	4.54	100
4	4.54	2.27	50
5	4.54	2.27	50
6	4.54	4.54	100
7	2.27	2.27	100
8	2.27	1.14	50

TABLE 3. Concentrations Measured in Third Dosed Tapwater Experiment

Compound	Tapwater	Dosed Tapwater (μg/L)	Effluent (μg/L)			Offgas (ng/L)
		D1	D1	D2	Avg	D1
Chloroform	20.2	101	97.1	97.3	97.2	3980
1,1,1-Trichloroethane	0.32	93.4	87.3	88.9	88.1	9520
Trichloroethylene	0.58	96	92.7	94.6	93.65	6920
Toluene	0.66	88.2	82.7	85.4	84.05	4980
Tetrachloroethylene	1.09	98.4	94.7	98	96.35	10700
o-Xylene	0.75	86.8	83.2	88.1	85.65	4710
1,4-Dichlorobenzene	0.58	82.1	81	85.3	83.15	2540
Bromoform	n.d.	62.1	63.2	61.5	62.35	728
1,1,2,2-Tetrachloroethane	n.d.	71.4	71.5	72	71.75	425
1,3,5-Trimethylbenzene	0.83	90.9	87.8	94.8	91.3	6100

ences between the influent and effluent liquid concentrations. In most cases the differences were less than the accuracy of the analytical method (approx. 5%). Therefore, only the gas phase measurements were employed in subsequent calculations to estimate the extent of volatilization from the process.

The data collected in the experiments were employed in mass balance analyses to assess the degree of mass closure, and to determine the extent of volatilization of the candidate compounds from the DAF. The former calculation was performed to assess the accuracy of the sampling and analytical techniques employed. A lack of mass closure would suggest a flaw in the techniques which would need to be improved upon. The latter allowed comparison of the volatilization of the target compounds in the absence of oils or other wastewater compounds to that observed in the subsequent experiments with wastewater.

The equation employed to assess mass closure was defined as:

$$\%Closure = 100 \times \frac{(Q_{sweep} \times C_g + Q_1 \times C_1)}{Q_0 \times C_0} \quad (10)$$

The percent of the candidate compounds that were volatilized from the DAF process were defined as:

$$\%Volatilized = 100 \times \frac{Q_{sweep} \times C_g}{Q_0 \times C_0} \quad (11)$$

An example of the results of the mass balance analyses for the dosed tapwater experiments is summarized in Table 4. The mass balance closures observed in the dosed tapwater experiments were, in general, not substantially different from 100%. The high degree of mass closure indicates that the DAF was operating at steady state and also suggests that precise sampling and analytical procedures were employed. It should be noted that, since the removal of the candidate compounds due to volatilization represented a relatively small fraction of the influent compounds, it was not valid to use the data to evaluate the accuracy of the measurements. In this scenario, even relatively large errors in the gas stream measurements would have only a minimal influence on the mass balance closure.

Tetrachloroethylene and 1,1,1-trichloroethane were volatilized to the greatest extent in the dosed tapwater experiments with the percent volatilized ranging from 2.16 to 3.38%. 1,1,2,2-Tetrachloroethane was volatilized to the least extent with the percent volatilized ranging from 0.14 to 0.18%. The data suggested a strong relationship between percent volatilized and the Henry's Law coefficient of the compounds, and hence Figure 2 presents a plot of the average percent volatilized in the tapwater experiments ver-

TABLE 4. Results of Dosed Tapwater Mass Balance Analyses for Experiment 2

Compound	Mass Balance Closure (%)	Volatilization (%)
Chloroform	98.1	1.04
1,1,1-Trichloroethane	102.8	2.63
Trichloroethylene	101.0	1.89
Toluene	99.1	1.45
Tetrachloroethylene	102.5	2.88
o-Xylene	100,1	1.41
1,4-Dichlorobenzene	103.2	0.86
Bromoform	105.4	0.33
1,1,2,2-Tetrachloroethane	100.7	0.18
1,3,5-Trimethylbenzene	103.1	1.82
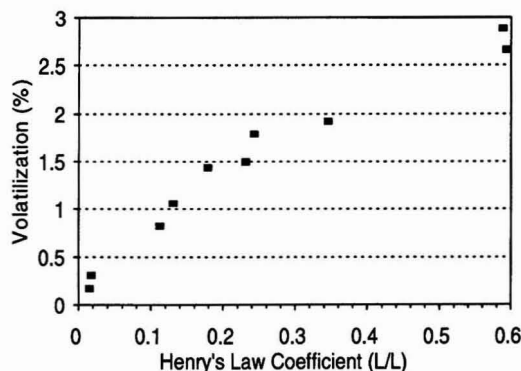
FIGURE 2 Percent volatilized vs Henry's law coefficient—tapwater experiments

TABLE 5. Summary of Wastewater Conventional Parameters

	Influent			Effluent			Float		
Exp	TSS (mg/L)	TVSS (mg/L)	Oil and Grease (mg/L)	TSS (mg/L)	TVSS (mg/L)	Oil and Grease (mg/L)	TSS (mg/L)	TVSS (mg/L)	Oil and Grease (mg/L)
1	49	15	595	17	7	37	19684	8108	11000
2	73	25	569	42	20	33	11404	8696	4140
3	127	38	120	60	26	89	14244	6956	8500
4	116	35	61	71	23	19	22180	8916	7500
5	121	38	36.5	34	9	11.5	29280	10300	1900
6	96	32	34.5	25	7	9.9	31648	11136	4360
7	30	11	43.3	16	2	7.7	2720	1548	3200
8	38	21	36.1	11	4	5.9	14588	8540	2530

sus the Henry's Law coefficient. Figure 2 indicates that over the range of Henry's Law values that were examined, the relationship deviates only slightly from linearity. A linear relationship between the percent volatilized and the Henry's law coefficient would suggest that the bubbles exiting the flotation basin were essentially saturated. This observation confirms the assumption of equilibrium partitioning to the bubbles that was employed in the model formulation.

DOSED WASTEWATER EXPERIMENTS

Conventional Parameters

Table 5 presents the total suspended solids (TSS), total volatile suspended solids (TVSS) and oil and grease concentrations measured in the DAF influent, effluent and float streams for each dosed wastewater experiment. It is apparent from Table 5 that the values of these parameters varied significantly over the period of the experimentation. The overall average removal of TSS and TVSS were 58 and 57% respectively. The suspended solids were substantially concentrated in the float, with concentrations generally 240 times higher than the influent levels. Table 5 also indicates that the DAF pilot plant was removing a substantial quantity of the oils, and that the oily materials were accumulating in the float. On average 74% of the influent oil and grease were removed through the DAF process. Float oil

and grease concentrations were on average 70 times higher than those observed in the process influent. These levels of removal are typical of DAF processes treating oil refinery wastewaters [11].

Candidate Compounds

Table 6 presents the measured concentrations of the candidate compounds in Experiment 8, which was conducted with low influent flow rate and a low recycle ratio. These results typify those obtained in the other experiments. In the dosed wastewater experiments, the candidate compounds were added to attain target concentrations of 100 µg/L, however, the measured concentrations of toluene, o-xylene and 1,3,5-trimethylbenzene were all considerably higher than the target concentrations. On average, the concentrations of toluene, o-xylene and 1,3,5-trimethylbenzene in the non-dosed wastewater were 3960, 980 and 190 µg/L respectively. This observation was not unexpected since these aromatic hydrocarbons are common constituents of untreated refinery wastewaters. Since there was substantial variability in the concentrations of these compounds, steady-state with respect to time could not be ensured, and hence, these compounds were eliminated from subsequent mass balance analyses.

An additional process stream, the float from the flotation basin was analyzed in the dosed wastewater experiments. The float samples were scraped from the surface of the

TABLE 6. Concentrations of Candidate Compounds in Wastewater in Experiment 8

Compound	Background Wastewater (µg/L)	Dosed Wastewater (µg/L)		Effluent (µg/L)		Float (µg/L)	Offgas (ng/L)	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 1	Sample 2
Chloroform	8.59	110	112	113	111	73.3	313	292
1,1,1-Trichloroethane	17.8	118	121	125	122	72	1790	1790
Trichloroethylene	0.42	107	113	132	126	77.1	1170	1140
Toluene	4000	3800	3650	3720	3280	2400	22300	20800
Tetrachloroethylene	0.86	99.8	105	101	98.1	118	2380	2420
o-Xylene	1000	930	878	935	824	1490	10300	9910
1,4-Dichlorobenzene	0.01	82	86.4	82.3	84	118	884	861
Bromoform	ND	84	86.2	84.8	85	4.87	179	160
1,1,2,2-Tetrachloroethane	ND	78.3	81.8	58.9	58.8	31.1	145	133
1,3,5-Trimethylbenzene	230	142	135	140	119	988	4480	4440

TABLE 7. Average Percent Volatilized in Dosed Wastewater Experiments

	Average Percent Volatilized			
	High Q	High Q	Low Q	Low Q
Compound	High R	Low R	High R	Low R
Chloroform	0.52	0.37	1.01	0.86
1,1,1-Trichloroethane	3.34	2.61	6.30	5.49
Trichloroethylene	2.17	1.60	4.08	3.68
Toluene	1.26	0.90	1.75	2.23
Tetrachloroethylene	5.18	4.26	8.46	9.85
o-Xylene	2.18	1.60	3.21	5.73
1,4-Dichlorobenzene	1.73	1.69	3.20	3.65
Bromoform	0.28	0.22	0.65	0.96
1,1,2,2-Tetrachloroethane	0.40	0.38	0.60	0.19
1,3,5-Trimethylbenzene	5.79	4.96	9.26	9.02

Q = Wastewater Flow Rate; R = Recycle Ratio

flotation basin upon completion of each experiment and consisted of a mixture of the oily substances present on the flotation basin surface and water which was entrapped in the float. On average, the concentrations measured in the float were 80% of those observed in the flotation basin effluent. It must be noted that, after collection these samples tended to separate into an oily layer which floated on top of the water during sample transport and storage. With the analytical techniques available it was only possible to analyze the contaminants present in the water layer. It is therefore suspected that some of the contaminants originally present in the water phase may have preferentially sorbed into the oily phase of these samples during storage. Since the rate of float production was small relative to the wastewater flowrate ($< 1\%$) the potential error in analysis of this stream was believed to have minimal influence on the conclusions that were obtained from this study.

Mass balance analyses were performed for the dosed wastewater experiments in a similar fashion to that employed for the dosed tapwater experiments. The mass balance closures ranged from 65.2 to 131.4%, with an overall average mass balance closure of 105%, indicating a high degree of mass balance closure in the eight experiments.

A high degree of replication was observed in the gas phase concentrations in the duplicate experiments (coefficient of variation $< 25\%$). Therefore, the average percent volatilized in the replicate experiments for each of the candidate compounds are presented in Table 7. It is apparent from Table 7 that the compound properties and process operating conditions had a substantial impact on the extent of volatilization measured from the DAF. The extent of volatilization observed in the pilot system ranged from 0.19% for 1,1,2,2-tetrachloroethane in the low flow-low recycle scenario to 9.85% for tetrachloroethylene in the low flow-low recycle scenario. The impact of wastewater flow rate on the percent volatilized is readily apparent. For virtually all of the compounds, the percent volatilized increased substantially when the wastewater flow rate was decreased. As an example, the volatilization of tetrachloroethylene increased from 5.18% to 8.46% for the high recycle conditions and from 4.26% to 9.85% for the low recycle conditions.

An analysis of variance (ANOVA) procedure was employed to statistically assess the impact of wastewater flow rate, recycle ratio and compound type on the stripping of the candidate compounds from the DAF. Due to the uncertainties in the influent concentrations of toluene, o-xylene, and 1,3,5-trimethylbenzene, the values for these compounds were not employed in the ANOVA procedure. The procedure indicated that influent flow rate and compound type had a significant effect on the extent of volatilization from the DAF. Effluent recycle did not have a statistically significant effect upon the extent of volatilization, however, the ANOVA procedure also indicated that there were significant interactions between the factors. For all compounds, the extent of volatilization was greater in the high flow-high recycle scenario as compared to the high flow-low recycle scenario. A similar trend was not apparent under the low flow condiitons.

The air emissions from the DAF likely result from a combination of surface volatilization and stripping to bubbles which rise through the flotation basin. Given the relatively low removal efficiencies observed in this study, the basin liquid concentrations did not vary substantially amongst experiments. Hence, the rate of surface volatilization would have been expected to have been relatively constant across the experiments. The differences in emissions that were observed therefore must have resulted from stripping to the bubbles. Under the conditions of low bubble production (low flow), the impact of varying the recycle rate, which directly influences the rate of bubble production, would be less than that under high flow conditions. Hence, with the variability in the data and the relative increase in importance of surface volatilization relative to stripping, the impact of varying recycle under low flow conditions could likely not be detected under the low flow conditions.

Model Application

The previously described model was evaluated by comparing estimates of the volatilization of the candidate compounds from the pilot DAF under each of the four operating conditions to the observed data. It should be noted that no calibration was performed with the experimental data to arrive at the emissions estimates.

The estimates are presented versus the observed values for each of the process operating conditions in Figures 3 to 6. The results presented in these figures would suggest that under all conditions of high wastewater flow and also for the condition of low wastewater flow with high recycle, the model was able to adequately predict the emissions of VOCs from the pilot DAF. This is reflected by the generally random distribution and minimal scatter of the residuals about the perfect fit line. Under the conditions of low wastewater flow and low recycle ratio the model tended to underpredict the emissions as compared to the observed values. Under these conditions, almost all of the observed values were greater than those predicted by the model.

To further investigate the modeling estimates, the predicted percent volatilized from the DAF was separated into that emitted as a result of air stripping and that emitted by surface volatilization. The values attributed to each mechanism are summarized in Table 8. With the exception of bromoform and 1,1,2,2-tetrachloroethane, under high flow and high recycle conditions, the surface volatilization contributed less than 10% of the overall emissions. Under low
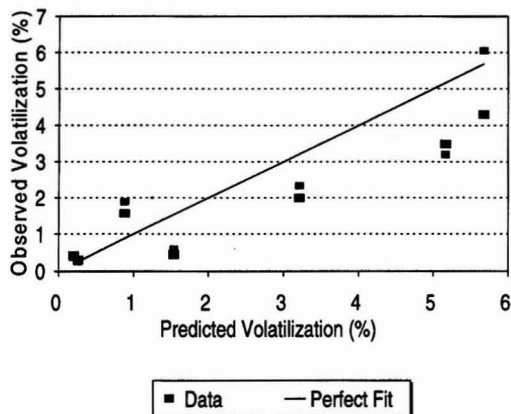
FIGURE 3 Observed vs predicted emissions; high flow—high recycle

FIGURE 4 Observed vs predicted emissions; high flow—low recycle

FIGURE 5 Observed vs predicted emissions; low flow—high recycle
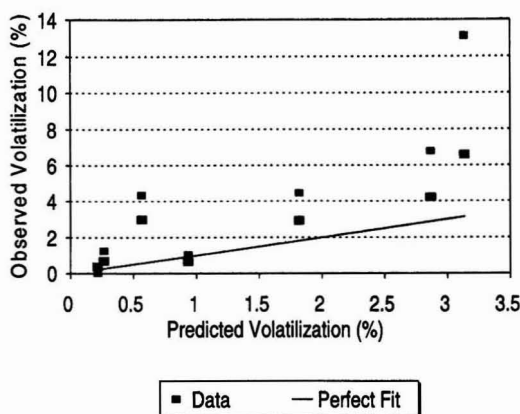
FIGURE 6 Observed vs predicted emissions; low flow—low recycle

flow and low recycle conditions, greater than 10% of the emissions, with the exception of tetrachloroethylene and 1,1,1-trichloroethane, resulted from surface volatilization. Four of the seven compounds that were examined had more than 20% of the emissions resulting from surface volatilization under low flow conditions.

The results would suggest that the error in the model would lie in the surface volatilization component. Under high flow and high recycle conditions, this component is relatively small and errors in this component would not be detectable. Under low flow and recycle conditions the contribution of surface volatilization is greater relative to the

TABLE 8. Volatilization from DAF by Mechanism

| | Relative Contribution of Mechanisms (%) to Total Emissions | | | | | | | |
| | High Q—High R | | High Q—Low R | | Low Q—High R | | Low Q—Low R | |
Compound	Bubble	Surface	Bubble	Surface	Bubble	Surface	Bubble	Surface
Chloroform	93.2	6.8	88.0	12.0	88.1	11.9	79.0	21.0
1,1,1-Trichloroethane	97.8	2.2	96.2	3.8	96.3	3.7	93.1	6.9
Trichloroethylene	96.7	3.3	94.2	5.8	94.2	5.8	89.3	10.7
Tetrachloroethylene	97.8	2.2	96.4	3.6	96.4	3.6	93.6	6.4
Bromoform	67.9	32.1	51.2	48.8	51.3	48.7	33.8	66.2
1,1,2,2-Tetrachloroethane	60.7	39.3	44.1	55.9	44.2	55.8	28.1	71.9
1,4-Dichlorobenzene	90.8	9.2	83.6	16.4	83.7	16.3	71.8	28.2

total stripping, and therefore, errors in this component of the model likely mask the effect of changing the recycle flow rate.

Based upon the results observed in the pilot plant, it would appear that the surface volatilization model underpredicts the emissions from this source. The underestimation of surface volatilization is inconsistent with the theoretical impact of the presence of an oil layer on the flotation basin surface. Theoretically, the oil layer would tend to reduce emissions since diffusivities would be lower and turbulence would be reduced in the more viscous liquid. Reduced diffusivities would result in a reduced overall mass transfer of VOCs. In the two-film theory of mass transfer, the lower level of turbulence would result in thicker mass transfer films, and hence, reduced mass transfer. However, the float which tends to accumulate on the surface of oil refinery dissolved air flotation basins is more of a foam than an oil layer. It may be that the foam acts to increase the effective surface available for mass transfer, and hence, the surface volatilization is greater than would be expected from even an open water surface. It is interesting to note that studies on auto-thermophilic aerobic digesters (ATAD) have demonstrated rates of oxygen mass transfer into digesting sludge that are greater than those attainable in clean water [12], [13]. It has been hypothesized that this increased rate of mass transfer results from mass transfer into the layer of foam which is typically observed on the surface of ATAD units. Further research is required to quantify this potential mechanism of mass transfer.

CONCLUSIONS

A pilot scale dissolved air flotation process was employed to assess the gas phase emissions of VOCs from dosed tapwater and dosed petroleum refinery wastewater. A high degree of mass balance closure was observed in the studies, however this primarily resulted from the relatively low removals which were generally below the variability in the liquid phase analyses. The fraction volatilized from the pilot DAF could only be quantified by measuring the off-gas mass flux of the candidate compounds.

The removals of suspended solids, oil and grease that were achieved in the pilot plant were typical of those observed in full scale treatment plants. Analysis of the liquid fraction of the float samples indicated some partitioning of the VOCs to oil may have occurred during sample transport and storage. Loss of the candidate compound to the float was believed to be a relatively minor removal mechanism.

Gas phase emissions of VOCs from DAFs are relatively low, ranging from 0.19% of 1,1,2,2-tetrachloroethane to 9.85% of tetrachloroethylene in this study. Hydraulic loading and compound type have a significant effect on emissions of VOCs from DAFs. Recycle had a greater effect on emissions at the higher hydraulic loading than at the lower loading.

A model which incorporated stripping by bubbles, volatilization from a quiescent oil-free surface and equilibrium partitioning to volatile solids and grease was developed. Saturation of the bubbles with respect to the liquid phase concentration and the compounds Henry's law coefficient was assumed.

The model was able to essentially simulate the candidate compound response under all experimental conditions ex-

cept the case with low hydraulic loading and low recycle rate. Under these conditions, surface volatilization had the greatest impact, although bubble stripping remained the primary removal mechanism for most compounds. It is believed that the surface volatilization model tends to underestimate the emissions from DAF surfaces. The cause of the underestimation may be the presence of the float in the form of a foamy layer. The high surface area of the foam would tend to increase liquid-gas mass transfer of the candidate compounds.

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Mass Transfer of Volatile Organics From Large Open Basins

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Controlling the volatilization of organic compounds from treatment works is becoming increasingly important as the definition of industrial categorical standards for air emissions by the EPA draws nearer. In this light, specific volatilization rates of several volatile organic compounds (VOC's) contained in multimillion gallon retention ("equalization basins") and settling ("primary clarifier") basins were measured using a flux chamber technique, a method used by the EPA for emission measurement. In this method, the liquid surface within an enclosing chamber is swept with air at a measured rate and the gas is analyzed. The mass transfer coefficients derived from these VOC vaporization rates were equal for the primary clarifier and the equalization basins. Factors were estimated to correct for the different ambient wind conditions to which these basins are exposed. Also it was determined that the rate of volatilization of VOC's with low Henry's law constants may be underestimated by the measurement. This is a result of the gas-phase resistance being dominant under the test conditions and the liquid-phase resistance being dominant under normal ambient conditions, and of the assumption that the liquid-phase resistance remains unchanged under both test and ambient conditions. The particular organics studied were acetone, methyl ethyl ketone, methyl isobutyl ketone, isopropanol, methanol and toluene.

SYSTEM

The Ciba-Geigy Corporation production plant in McIntosh, Alabama operates an above-ground biological Wastewater Treatment System. It is used to oxidize biologi-

cally the various wastewaters discharged by the production facilities on the site. The treatment includes neutralization, primary clarification, equalization, biological oxidation, secondary clarification, and sand filtration.

VOC emissions were measured at the primary clarifier and the equalization basins. The primary clarifier has a diameter of 27.4 meters (90 ft) and has a volume of 3028 cubic meters (800,000 gallons). It is equipped with rake arms rotating at approximately 1.3 revolutions per minute. The supernatant from the primary clarifier flows by gravity into two rectangular equalization basins each 24.4 meters (80 ft) wide by 104.3 meters (342 ft) long and with walls 9.1 meters (30 ft) high. The liquid depth in these basins is maintained near 6.5 meters (21.5 ft), so that the liquid volume in each basin is approximately 16,600 cubic meters (4.4 million gallons). The basins are stirred by two 20 HP submersible mixers in each basin. The contents are well mixed as determined by an analysis of inlet and outlet concentration variations.

The liquid flow through the system is approximately 13,200 cubic meters per day (3.5 million gallons per day), all of which flows through the primary clarifier and half of which flows through each of the two equalization basins. The basins are partially covered, and the head space is about 2.6 meters (8.5 feet).

The wind velocity around the system typically ranges between 0.6 and 4.4 meters/sec (1 to 9 mph). The liquid in the primary clarifier is exposed to the wind. The liquid surface in the equalization basins is protected from the wind by the high walls of the basin, so that the wind velocity measured above the liquid surface at different positions over the equalization basins was found to range between 0.2 and 0.3 meters/sec (0.5 to 0.7 mph). The direction of the wind was not ascertained. The temperature in the basins

varies with the season. During the period of the study it averaged 25°C.

The major VOC's treated in the system are acetone, methyl ethyl ketone, methyl isobutyl ketone, isopropanol, methanol, and toluene. Other VOC's, such as xylenes, n-butanol and ethanol, are also processed by the system but at significantly lower concentrations.

BACKGROUND

The two-film concept used in correlating multiphase mass transfer has been recognized for many years as a useful tool to correlate vaporization rates from bodies of water [1, 2]. This method postulates that vaporization occurs in two steps: transfer from the liquid phase to the interface followed by transfer from the interface to the air. Vaporization rates are calculated using mass transfer coefficients estimated for the liquid and gas phases. Reliable mass transfer coefficients are normally unavailable for real systems, even though a number of correlations for estimating them have been proposed based on simplifying assumptions.

In practice, by assuming simple geometries and idealizing the air flow patterns within the system, the gas-phase transfer coefficients may be estimated using some of the generalized correlations available in the field of chemical engineering. Liquid-phase coefficients from large bodies of liquid, however, are more difficult to predict since there are few data in the literature on mass transfer in such systems. Some dimensional correlations have been proposed for VOC vaporization from large bodies of water, but there is limited experience on their reliability.

Mass Transfer Coefficients

The two-film concept is based on a two-step mechanism. In vaporizing from an aqueous basin, a VOC is transferred from the bulk of the aqueous phase (the contents of the basins) to the bulk of the gas phase (the atmosphere) in two steps: it is first transferred from the bulk of the liquid to the vapor-liquid interface (the liquid phase mass transfer step) then from the interface to the bulk of the vapor (the gas phase mass transfer step). The mass transfer coefficients corresponding to these two mechanisms are defined as [1]:

$$k_L = \frac{\left(\begin{array}{c}\text{Rate of Vaporization of Organic}\\\text{Compound, moles/time}\end{array}\right)}{\text{Surface Area} \times \text{Molar Liquid Density} \times (X_L - X_i)}$$
(1a)

and,

$$k_G = \frac{\left(\begin{array}{c}\text{Rate of Vaporization of Organic}\\\text{Compound, moles/time}\end{array}\right)}{\text{Surface Area} \times \text{Molar Air Density} \times (Y_i - Y_G)}$$
(1b)

(The symbols are explained in the Notation section at the end of the article.) At the vapor-liquid interface, the concentrations of the VOC in the vapor and in the liquid are related together by the thermodynamics of vapor-liquid equilibrium. At low solute concentrations, the vapor-liquid equilibrium can be expressed in terms of Henry's law:

$$p_i = P \times Y_i = H \times X_i$$
(2)

An over-all mass transfer coefficient, K_L, based on the liquid phase driving force is defined as:

$$K_L = \frac{\left(\begin{array}{c}\text{Rate of Vaporization of Organic}\\\text{Compound, moles/time}\end{array}\right)}{\text{Surface Area} \times \text{Molar Liquid Density} \times (X_L - [Y_G \times P/H])}$$
(3)

The three mass transfer coefficients expressed above are all related together by the equations,

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{\text{Liquid density } (\rho_L) \times P}{\text{Air density } (\rho_G) \times k_G \times H}$$
(4)

This equation represents the resistances to mass transfer: the total resistance being the sum of the liquid- and the gas-phase resistances. Using these relationships, the rate of vaporization of a VOC from a specific system can be calculated when the vapor-liquid equilibrium is known and the mass transfer coefficients can be estimated.

It is common chemical engineering practice to estimate the mass transfer coefficients of simple systems from empirical correlations which relate the liquid- and gas-phase mass transfer coefficients to the system conditions and fluid properties. For both the aqueous and air phases these correlations are usually of the form:

Sherwood no. $= f$ (Reynolds no., Schmidt no.)

$$= constant \times (Reynolds\ no.)^a \times (Schmidt\ no.)^b$$

$$(k \times L/D) = constant \times (\rho VL/\mu)^a \times (\mu/\rho D)^b$$
(5)

k and D refer to the mass transfer coefficient and the diffusivity respectively (gas or liquid). L represents a characteristic dimension of the system; V represents a velocity (wind for the gas phase and liquid velocity for the aqueous phase). The exponent "b" on the Schmidt number is typically 1/3 [1].

One such correlation, applicable to the gas phase of the equalization basins is the Chilton-Colburn analogy as expressed by Rohsenow and Choi [3] for turbulent tangential flow over a flat surface. The mass transfer coefficient averaged over the length of the surface is:

Sherwood no. $= (k_G \times L/D_G)$

$$= 0.037 \times (Schmidt\ no.)^{1/3} \times \{(Reynolds\ no.)^{0.8} - 15,500\}$$
(6)

No similar dimensionless relationship has been developed for estimating the liquid-phase mass transfer coefficients at the surface of large basins.

Dimensional relationships for both mass transfer coefficients have been proposed by a number of investigators. In the environmental field, mass transfer coefficients have been related to various environmental conditions. A review of some of these methods is given in Lyman et al. [2] in which a number of approaches by different investigators are described. For example, Southworth [4] proposed equations for the mass transfer coefficients in the vaporiza-

tion of polyclic aromatic hydrocarbons. Of interest is the relationship for the gas-phase mass transfer coefficient:

$$k_G \, (\text{cm/sec}) = 1{,}137.5 \times (V_{\text{wind}} + V_L) \times (18/M)^{0.5} \quad (7)$$

where V_{wind} and V_L represent the wind and the liquid stream velocities in m/sec, and M is the molecular weight of the VOC. In this relationship, the diffusivity of the VOC in air is defined by the molecular weight.

Also, Cohen et al. [5] proposed liquid-phase mass transfer coefficients from bodies of water in the presence of wind waves. They propose using three wind speed regions: below 3 m/sec (about 6 mph), when the liquid-phase mass transfer coefficient is strongly influenced by the liquid turbulence; between 3 and 10 m/sec, when wind-induced waves control the mass transfer, and above 10 m/sec, when whitecapping may occur.

At wind speeds below 3 m/sec, which is the region of interest here,

$$k_L \, (\text{cm/sec}) = 1 \text{ to } 3 \text{ cm/hour}$$

$$= 0.00028 \text{ to } 0.00083 \text{ cm/sec} \quad (8)$$

At higher wind speeds, representing the other two regions, k_L is strongly influenced by the wind.

Flux Chamber Method

The flux chamber technique was developed to measure VOC vaporization rates directly without resorting to any correlation for estimating mass transfer coefficients.

The method used in this study is similar to the one described by Gholson et al. [6]. The flux chamber consisted of an inverted Tedlar-lined bucket placed over the surface of the liquid. Its diameter was 37.5 cm, and its volume was approximately 55 liters. In order to avoid distorting the liquid flow pattern, the rim of the bucket was placed just below the surface providing a seal without significantly disturbing the liquid. Air was introduced into the chamber via a distribution ring and flowed out through a flow meter. Provisions were made to collect in a Tedlar bag a sample of the air flowing through the chamber. This sample was then analyzed by gas chromatography as required. A diagram of the system is shown in Figure 1. The air flow was set at about 7 liters per minute.

The VOC concentrations in the gas collected were analyzed periodically until a steady state was reached. Based on the steady state VOC concentrations, the air flow rate and the surface areas of the basin and of the liquid covered by the chamber, the vaporization rate from the basin was calculated.

Even though the flux chamber technique was developed to measure VOC vaporization rates directly and to avoid the uncertainties in using a simplified physical model it is inherently based on another assumption: that the data gathered during the measurement truly represent vaporization under normal ambient conditions and that the controlling resistances in the vaporization are equal in both test and under ambient conditions. If this assumption is not valid, the measured rates will differ from actual vaporization rates.

If the chamber is assumed not to disturb the liquid flow patterns, the liquid-phase mass transfer coefficient mea-
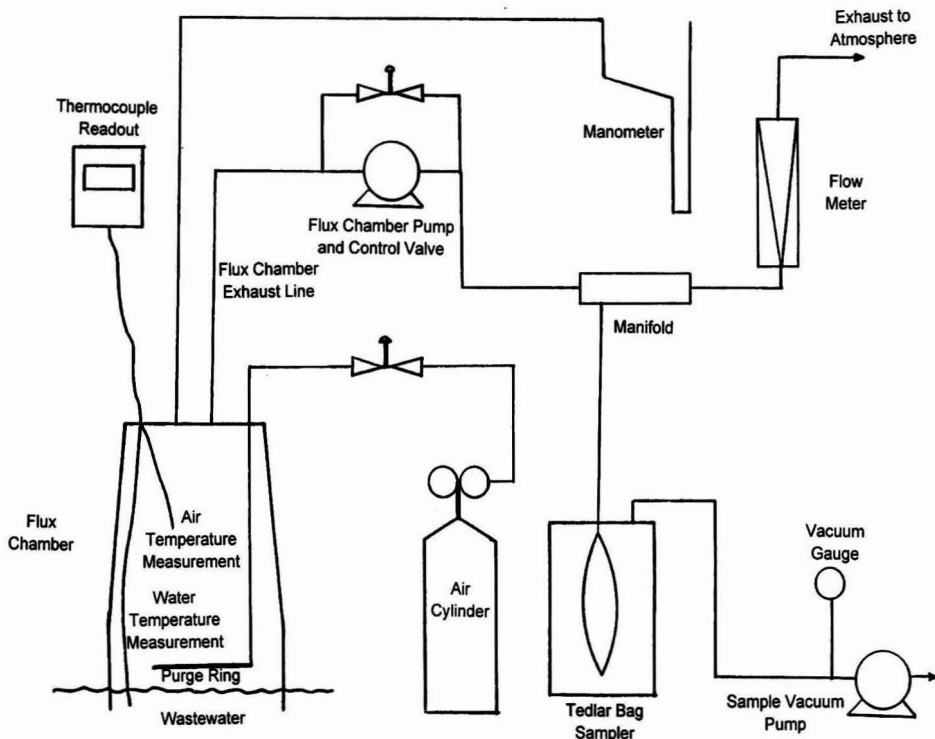
FIGURE 1 Schematic diagram of the flux chamber sampling system.

sured by the flux chamber technique will be equal to the ambient condition coefficient. The environment in the gas phase during the measurement, however, may be significantly different from normal ambient conditions. If this is so, then the measured gas-phase coefficient will be different from the one under normal ambient conditions.

DATA REDUCTION METHOD

Determination of the Mass Transfer Coefficients

The six VOC's considered in this study vaporize simultaneously from the system. Except for the diffusivities and vapor-liquid equilibria which differ, the physical properties, the geometry and the flow parameters of the system are identical for all six VOC's. The mass transfer coefficients for the system can then all be expressed in terms of dimensional relationships derived from equation (5):

$$k_L = \beta_L \times D_L^{1-b} \qquad (9a)$$

and,

$$k_G = \beta_G \times D_G^{1-b} \qquad (9b)$$

The symbol β_L is a constant for this system and refers to geometry, flow and property terms characteristic of the liquid phase of the system. Similarly, the symbol β_G refers to terms representing the gas phase.

Contrary to the liquid-phase mass transfer coefficient which may be assumed to be unaffected by the measurement process, the measured gas-phase mass transfer coefficient depends upon the conditions of the vaporization rate measurement and is not truly characteristic of the system. To differentiate between measured values dependent upon the measurement procedure and values referring to true characteristics of the system, the terms resulting from measurement will be denoted with a superscript $'$, so that:

$$k_L' \approx k_L = \beta_L \times D_L^{1-b} \qquad (10a)$$

$$k_G' = \beta_G' \times D_G^{1-b} \qquad (10b)$$

Substituting for k_L' and k_G' from equations (9) into equation (4) we have:

$$\frac{1}{K_L'} = \frac{1}{\beta_L D_L^{1-b}} + \frac{\rho_L}{\rho_G \beta_G' D_G^{1-b}} \cdot \left(\frac{P}{H}\right) \qquad (11)$$

Rearranging,

$$\frac{D_L^{1-b}}{K_L'} = \frac{1}{\beta_L} + \frac{\rho_L}{\rho_G \beta_G'} \cdot \left(\frac{P}{H} \cdot \left(\frac{D_L}{D_G}\right)^{1-b}\right) \qquad (12)$$

For a given configuration in which the system geometry, flow conditions and temperature are unchanging, the term (D_L^{1-b}/K_L') can be plotted against the term $\{P/H \cdot (D_L/D_G)^{1-b}\}$ for the different VOC's, and a straight line is obtained. Its intercept is $1/\beta_L$ and its slope is $\rho_L/(\rho_G \beta_G')$. From the intercept and the slope, the mass transfer coefficients for the system under the conditions of the measurement can be determined.

Estimation of Ambient Vaporization Rates— Determination of Mass Transfer Resistances

The rate of vaporization of a VOC under ambient conditions is set by the over-all resistance to mass transfer in the system, i.e., by the sum of the ambient liquid-phase and the gas-phase mass transfer resistances. This was defined in equation (4) as $1/K_L$.

Under the conditions of the measurement, the over-all resistance, $1/K_L'$, is defined by the measured values of k_L' and k_G'. Under ambient conditions the over-all resistance is defined by the ambient values of k_L and k_G. As stated above, the liquid-phase mass transfer coefficient is assumed to be equal to the flux chamber measurement value, but the gas-phase coefficient depends on the ambient conditions and must be determined by other means, such as one of the correlations available for example from equations (6) or (7). A correction factor "F" may be defined as

$$F = \text{measured resistance/estimated ambient resistance}$$

$$= \frac{\{1/k_L + [1/k_G' \cdot \rho_L/\rho_G \cdot P/H]\}}{\{1/k_L + [1/k_{G\text{-}correl} \cdot \rho_L/\rho_G \cdot P/H]\}} \qquad (13)$$

The corrected rate of vaporization under ambient conditions may then be estimated from the measured rate of VOC vaporization:

$$\text{Corrected rate} = \text{Measured rate} * \text{Correction factor "}F\text{"} \qquad (14)$$

It is useful to define a measure for the degree of gas-phase control. This is the ratio of gas-phase resistance to the total resistance. Using the appropriate mass transfer coefficients,

$$\text{Gas-phase control} = \frac{K_L}{k_G} \cdot \frac{\rho_L}{\rho_G} \cdot \frac{P}{H}$$

$$= \frac{[1/k_G \cdot \rho_L/\rho_G \cdot P/H]}{\{1/k_L + [1/k_G \cdot \rho_L/\rho_G \cdot P/H]\}} \qquad (15)$$

If, under the conditions of measurement, this ratio is small (say less than 0.1), then the liquid-phase resistance is dominant and the gas-phase resistance plays only a minor role in defining the rate of vaporization. Measured rates will then be equal to ambient vaporization rates over a wide range of conditions. At the higher degrees of gas-phase control, the gas-phase resistance affects the rate of vaporization and it is necessary to calculate the correction factor "F" and to determine the magnitude of correction needed.

Significant corrections are required only when the gas-phase resistance is dominant and the values of k_G and k_G' differ.

RESULTS

Equalization Basin

Mass Transfer Coefficients

The results of measurements on the equalization basin are summarized in Table 1. The table shows the over-all

TABLE 1. Measured Vaporization Losses from the Equalization Basin

VOC	Aqueous Conc'n (mg/liter)	Rate Vaporiz'n (gm/hour)	K'_L (cm/sec)
E-basin			
Toluene	17.3	1014	6.66E-04
MEK	37.5	284	8.57E-05
MIBK	8.7	52	6.74E-05
Acetone	42.2	170	4.56E-05
iPOH	276	370	1.52E-05
MeOH	427	262	6.94E-06
W-basin			
Toluene	13.8	933	6.98E-04
MEK	54	374	7.13E-05
MIBK	8.5	80	9.67E-05
Acetone	42	162	3.96E-05
iPOH	253	329	1.34E-05
MeOH	536	251	4.82E-06

measured coefficient K'_L for methanol, MEK, acetone, MIBK isopropanol and toluene.

Typically, the exponent "b" on the Schmidt number in equation (5) is 1/3. Using that value for the exponent, the term ($D_L^{2/3}/K'_L$) is plotted against [$P/H \cdot (D_L/D_G)^{2/3}$] in Figure 2 for the six solutes.

Error limits (equal to the total standard error from all major sources, $\pm 26\%$ of the vaporization rate—see Appendix) are shown around each data point to reflect the combined standard errors on each measurement and physical property. The regression line and the 95% prediction band (confidence limits of points around the line) are shown in Figure 2. The regression line was forced through the average data for toluene to ensure that it represents well the points with high values of H near the origin (i.e. points with liquid-phase control). That linear regression shows a good correlation ($r = 0.913$ with 10 degrees of freedom; $r_{99\%} = 0.765$, for 99% significance).

The regression line has an intercept of $1/\beta_L = 0.636$ and a slope of $\rho_L/(\rho_G \beta'_G) = 1.05 \times 10^5$ in cgs units. For the equalization basins, the measured mass transfer coefficients for the VOC's are then calculated to be:

$$k'_L \,(\text{cm/sec}) = 1.57 \times \left\{ D_L \left(\text{cm}^2/\text{sec} \right) \right\}^{2/3} \quad (16a)$$

and,

$$k'_G \,(\text{cm/sec}) = 0.130 \times \left\{ D_G \left(\text{cm}^2/\text{sec} \right) \right\}^{2/3} \quad (16b)$$

The above calculations were repeated with different values of the exponent "b," between 0 and 1 (Table 2). Even though the correlation coefficient increased steadily from $b = 0$ (mass transfer coefficient directly proportional to the diffusivities, as in equation (7) above) to $b = 1$ (mass transfer coefficients independent of diffusivities, as in equation (8) above), these differences were not statistically significant on the 95% significance level, and the generally accepted value of $b = 1/3$ will continue to be used here.

Based on average diffusion coefficients of $D_L = 10^{-5}$ cm²/sec and $D_G = 0.1$ cm²/sec (see Table A), average mass transfer coefficients were estimated. These are:
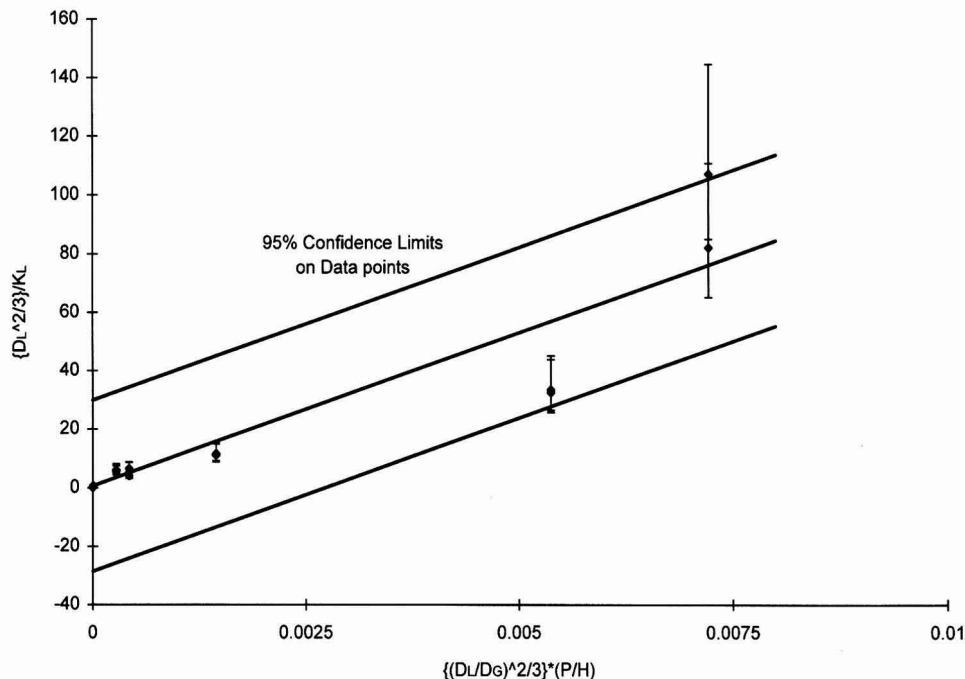
FIGURE 2 Mass transfer relationship for the equalization basins ("b" = 1/3).

TABLE 2. Correlation Coefficients for Exponents "b" in Equation (5)

(99% Significance level of r with 10 degrees of freedom = 0.765)

Value of Coefficient "b"	r^2	Correlation Coefficient (r)
0	0.794	0.891
1/3	0.833	0.913
0.5	0.852	0.923
1.0	0.900	0.949

$$k'_{L(Average)} = 0.00073 \text{ cm/sec}$$

$$\approx k_L$$

and

$$k'_{G(Average)} = 0.028 \text{ cm/sec.}$$

Note that the value of $k'_{L(Average)} (\approx k_L)$ agrees with the results of Cohen et al. [5] falling near their upper limit at low air velocities with an agitated liquid.

Estimation of Gas-phase Control

The degree of gas-phase control for each individual VOC during the measurement was estimated from equation (15), using $k'_{L(Average)}$ and $k'_{G(Average)}$. The results are shown in Table 3. As expected, the liquid-phase resistance during the test dominates the vaporization of toluene, the VOC with the highest Henry's law constant. Its vaporization rate is essentially independent of the gas-phase conditions.

Table 3 also shows that under the conditions of the measurement more than 80% of the resistance is governed by the gas phase when the Henry's law constant is less than about 8.2 atmospheres. The measured vaporization rates of methanol, isopropanol, methyl isobutyl ketone, methyl ethyl ketone and acetone are therefore all gas-phase controlled.

To determine the degree of gas-phase mass transfer resistance in the gas under ambient conditions, it is necessary to estimate the ambient gas-phase transfer coefficients. The Rohsenow and Choi correlation [3] equation (6), and the Southworth relationship [4] equation (7), were used for that purpose. Assuming a representative wind velocity of 0.6 mph (about 30 cm/sec) blowing across the width or along the length of the equalization basins (24.4 m and 104.3 m, respectively), the value of k_G was calculated from the Rohsenow and Choi correlation [3]. With an average Schmidt number of 0.8,

$$k_{G\text{-Rohsenow \& Choi}} = 0.022 \text{ and } 0.028 \text{ cm/sec,}$$

(for the wind blowing across the width or along the length of the basins, respectively). Also, for a VOC with a typical molecular weight of 60, the Southworth relationship [4] gives:

$$k_{G\text{-Southworth}} = 0.044 \text{ cm/sec.}$$

In this system the values calculated from the Rohsenow and Choi correlation [3] are insensitive to the characteristic dimension. Also the Rohsenow and Choi correlation [3] gives lower average values of the mass transfer coefficient than the Southworth [4] relationship; the two sets of values are expected to bracket a representative ambient gas-phase coefficient.

The measured value of $k'_{G(Average)}$ determined above is seen to be within the uncertainty of the estimates of the ambient gas-phase coefficient. The gas-phase resistances (and degree of gas-phase control) under the conditions of the measurement are therefore essentially the same as the ambient ones.

At higher wind velocities the difference between the expected and measured gas-phase transfer coefficients, however, widens. For example at a wind velocity of 2 mph, we have:

$$k_{G\text{-Rohsenow \& Choi}} = 0.098 \text{ and } 0.084 \text{ cm/sec,}$$

and

$$k_{G\text{-Southworth}} = 0.15 \text{ cm/sec.}$$

These values are significantly higher than the measured gas-phase mass transfer coefficients and the gas-phase control will change. The differences between the estimated gas-phase control under ambient conditions and during measurement are shown in Table 3.

Toluene remains completely liquid-phase controlled within the range of wind velocities expected. The other VOC's are mostly gas-phase controlled at the lowest wind speed. Methyl ethyl ketone and methyl isobutyl ketone,

TABLE 3. Gas-Phase Control in the Vaporization of VOC's from the Equalization Basins under Different Conditions
(For Wind Speeds of 0.6, 1 and 2 mph)

VOC	Flux Chamber	Wind = 0.6 mph Rohsenow Wind Along/Across	South-worth	Wind = 1 mph Rohsenow Wind Along Basin	Rohsenow Wind Across Basin	South-worth	Wind = 2 mph Rohsenow Wind Along Basin	Rohsenow Wind Across Basin	South-worth
Toluene	0.08	0.10	0.05	0.05	0.05	0.03	0.03	0.02	0.02
MEK	0.81	0.85	0.74	0.73	0.72	0.61	0.59	0.56	0.44
MIBK	0.87	0.89	0.80	0.79	0.79	0.70	0.68	0.65	0.54
Acetone	0.96	0.97	0.94	0.93	0.93	0.90	0.89	0.87	0.81
iPOH	0.99	0.99	0.98	0.98	0.98	0.97	0.97	0.96	0.94
MeOH	0.99	0.99	0.99	0.99	0.99	0.98	0.98	0.97	0.96

TABLE 4. Correction Factors for VOC Vaporization Rates in the Equalization Basins
(For Wind Speeds of 0.6, 1 and 2 mph)

VOC	Wind = 0.6 mph		Wind = 1 mph			Wind = 2 mph		
	Rohsenow Wind Along/Across	South-worth	Rohsenow Wind Along Basin	Rohsenow Wind Across Basin	South-worth	Rohsenow Wind Along Basin	Rohsenow Wind Across Basin	South-worth
Toluene	0.98	1.03	1.03	1.03	1.05	1.06	1.06	1.07
MEK	0.82	1.42	1.48	1.49	2.08	2.20	2.39	3.00
MIBK	0.81	1.45	1.52	1.54	2.23	2.38	2.62	3.43
Acetone	0.79	1.53	1.62	1.64	2.57	2.80	3.19	4.66
iPOH	0.79	1.55	1.65	1.67	2.70	2.96	3.41	5.24
MeOH	0.79	1.56	1.65	1.67	2.72	2.98	3.44	5.32

with the next highest Henry's law constants, show some liquid-phase control which becomes more pronounced as the wind speed increases. Methanol, with the lowest Henry's law constant, remains gas-phase controlled throughout the whole range of wind speeds.

Correction of Measured Rates

Correction factors "F" were calculated for different ambient conditions. Both the Rohsenow and Choi [3] correlation (assuming winds blowing across and along the basins) and the Southworth [4] relationship were again used to estimate ambient gas-phase coefficients at 0.6 mph, 1 mph and 2 mph wind velocities. Calculated values of the correction factor "F" are shown in Table 4 and in Figure 3.

As expected, no adjustment is necessary for toluene. Regardless of wind conditions the vaporization of toluene is liquid-phase controlled. Methanol, which has the lowest Henry's law constant of the VOC's in the system, has the highest degree of gas-phase control, so that when ambient conditions differ from measurement conditions it requires the greatest correction. Its correction factor is also the most sensitive to ambient conditions and to the estimated value of the gas-phase coefficient.

PRIMARY CLARIFIER

VOC vaporization rates from the primary clarifier were also measured using the flux chamber. In this study, the aqueous VOC concentrations in the clarifier were not measured directly. They were determined from the VOC
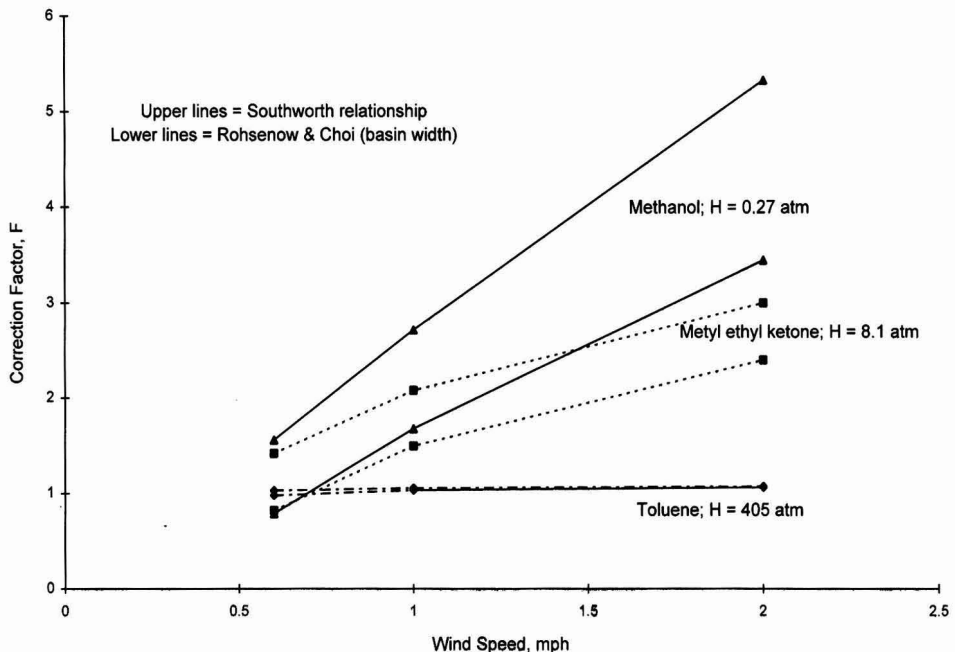
FIGURE 3   Effect of wind speed on correction factor (based on the Rohsenow and Choi correlation and the Southworth relationship).

	Aqueous Conc'n (mg/liter)	Rate Vaporiz'n (gm/hr)	K'_L cm/sec
Primary Clarifier			
Toluene	6.9	96	7.00E-04
MEK	52.5	114	1.09E-04
MIBK	8.8	14	7.96E-05
Acetone	47.3	41	4.35E-05
iPOH	249.3	80	1.61E-05
MeOH	547.3	70	6.42E-06

concentrations measured in the equalization basins after adjusting for their losses to the atmosphere. (Note that these determinations were not made during the equalization basin measurements but during other days with different equalization basin VOC concentrations. The losses were assumed to follow the Rohsenow and Choi [3] correlation with a 0.6 mph wind velocity.) The adjustments to the concentrations were minor. From these data, over-all mass transfer coefficients were calculated, similarly to the equalization basins. The results are listed in Table 5.

The mass transfer data were reduced similarly to the equalization basins. Figure 4 shows the primary clarifier data together with the regression line and confidence limits representing the equalization basin. These data show good agreement with the equalization basin measurements, falling within the 95% confidence limits. As expected, the measured liquid- and gas-phase mass transfer coefficients of the primary clarifier and the degree of gas-phase control are consistent with those of the equalization basins, since

the liquid coefficients for both vessels are approximately equal [equation (8)], and the gas coefficients are determined under the same test conditions.

Under ambient conditions, the primary clarifier is exposed to higher winds than the equalization basins, and its gas-phase mass transfer coefficient under these conditions are expected to be significantly higher than that of the equalization basins. Higher correction factors are expected.

No simple chemical engineering correlation is known for estimating gas-phase mass transfer coefficients for the clarifier. If the Rohsenow and Choi [3] correlation is used, assuming the clarifier diameter (87 ft) to be the characteristic dimension, then at typical wind velocities of 1 to 5 mph, the mass transfer coefficients in the gas phase are:

$$k_{G\text{-Rohsenow \& Choi}} = 0.098 \text{ to } 0.23 \text{ cm/sec.}$$

If the Southworth [4] relationship is used, the mass transfer coefficients at 1 to 5 mph are:

$$k_{G\text{-Southworth}} = 0.15 \text{ to } 0.38 \text{ cm/sec.}$$

The degree of gas-phase control was calculated (Table 6) and corrections to measured vaporization rates were applied similarly to the equalization basins. Owing to the higher wind velocities to which the primary clarifier is exposed, its correction factors where gas-phase is controlling are considerably higher than those for the equalization basins. These are shown in Table 7.

CONCLUSIONS

Liquid- and gas-phase mass transfer coefficients were measured at the equalization basins and at the primary
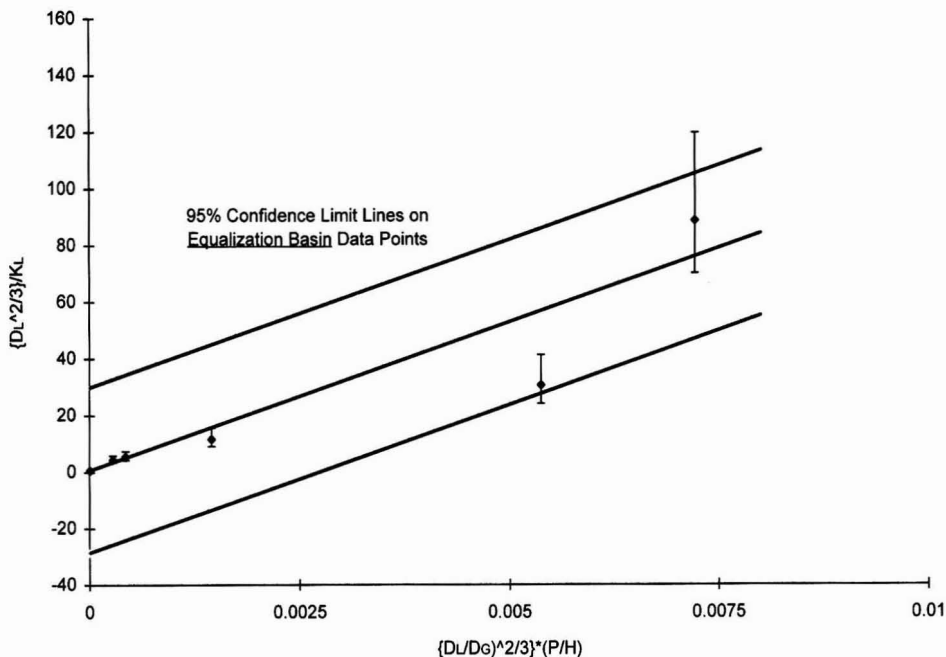
FIGURE 4 Mass transfer relationship for the primary clarifier ("b" = 1/3).

TABLE 6. Gas-Phase Control in the Vaporization of VOC's from the Primary Clarifier under Different Conditions
(For Wind Speeds of 2, 5 and 10 mph)

VOC	Flux Chamber	Wind = 2 mph		Wind = 5 mph		Wind = 10 mph	
		Rohsenow & Choi	Southworth	Rohsenow & Choi	Southworth	Rohsenow & Choi	Southworth
Toluene	0.08	0.02	0.02	0.01	0.01	0.01	0.00
MEK	0.81	0.56	0.44	0.35	0.24	0.23	0.14
MIBK	0.87	0.65	0.54	0.44	0.32	0.31	0.19
Acetone	0.96	0.87	0.81	0.75	0.63	0.75	0.63
iPOH	0.99	0.96	0.94	0.92	0.86	0.86	0.76
MeOH	0.99	0.97	0.96	0.94	0.90	0.90	0.82

TABLE 7. Correction Factors for VOC Vaporization Rates in the Primary Clarifiers
(For Wind Speeds of 2, 5 and 10 mph)

VOC	Wind = 2 mph		Wind = 5 mph		Wind = 10 mph	
	Rohsenow & Choi	Southworth	Rohsenow & Choi	Southworth	Rohsenow & Choi	Southworth
Toluene	1.06	1.07	1.08	1.08	1.08	1.08
MEK	2.39	3.00	3.49	4.08	4.14	4.64
MIBK	2.62	3.43	4.13	5.06	5.15	6.02
Acetone	3.18	4.66	6.28	9.09	9.42	13.31
iPOH	3.40	5.24	7.47	12.02	12.63	21.15
MeOH	3.44	5.32	7.65	12.53	13.20	22.86

clarifier. As expected, the liquid-phase coefficients in all basins were found to be equal, since these coefficients are insensitive to liquid mixing in the basins. The gas-phase mass transfer coefficients were also found to be equal, since the coefficients determined by the flux chamber method do not reflect the differences in the ambient air conditions to which these vessels are exposed but only reflect the conditions within the test chamber.

A correction must then be applied to the measured gas-phase coefficients to adjust for wind conditions. In this study, the primary clarifier is exposed to higher winds than the equalization basins and the correction to its gas-phase mass transfer coefficients is expected to be significantly higher than those of the equalization basins. The correction to the gas-phase mass transfer coefficients results in another correction to the vaporization rates; this latter correction is major for VOC's whose vaporization is gas-phase controlled (i.e., those with low Henry's law constants) but unimportant for VOC's with high Henry's law constants.

To estimate the correct vaporization rates from measured rates, it is necessary to estimate the gas-phase transfer coefficients under ambient conditions. In this study, two correlations for estimating the gas-phase coefficients were used. As may be expected, that correction is sensitive to the estimated gas-phase coefficients for VOC's with low Henry's law constants (e.g., methanol and isopropanol).

For the range of diffusivities covered in this study, the measured liquid- and gas-phase mass transfer coefficients averaged:

$$k'_L \text{ (cm/sec)} = 0.00073 \text{ cm/sec}$$

and

$$k'_G \text{ (cm/sec)} = 0.028 \text{ cm/sec}$$

The liquid-phase mass transfer coefficients reflect actual vessel characteristics, but the gas-phase coefficients represent the conditions of the measurement. In practical applications it is critical to understand the limitations of the test procedure described in this paper.

NOTATION

a = exponent on the Reynolds number in the generalized mass transfer correlations
b = exponent on the Schmidt number in the generalized mass transfer correlations
D_L, D_G = diffusion coefficients of the VOC in the liquid and in the air (cm²/sec)
F = correction factor, total resistance to mass

transfer during test/total resistance under ambient conditions

H = Henry's law constant, units of pressure

K_L = over-all mass transfer coefficient under ambient conditions, based on the concentration of the VOC in solution (cm/sec = moles/sec/(moles/cm^3)/cm^2)

K'_L = over-all mass transfer coefficient based on the concentration of the VOC in solution determined during the vaporization rate measurement (cm/sec)

k_L = liquid-phase mass transfer coefficient for transfer from the bulk of the liquid to the vapor-liquid interface (cm/sec)

k_G = true gas-phase mass transfer coefficient for transfer from the vapor-liquid interface to the bulk of the air space (cm/sec) under ambient conditions

$k_{G\text{-system}}$ = gas-phase mass transfer coefficient for transfer from the vapor-liquid interface to the bulk of the air space (cm/sec) estimated from a generalized correlation

$k_{G\text{-Rohsenow \& Choi}}$ = gas-phase mass transfer coefficient estimated from the Rohsenow & Choi correlation (cm/sec)

$k_{G\text{-Southworth}}$ = gas-phase mass transfer coefficient estimated from the Southworth relationship (cm/sec)

k'_G = gas-phase mass transfer coefficient for transfer from the vapor-liquid interface to the air space estimated from the flux chamber measurement (cm/sec)

k'_L = liquid-phase mass transfer coefficient for transfer from the liquid to the vapor-liquid interface estimated from the flux chamber measurement (cm/sec)

L = characteristic dimension of the system

M = molecular weight of the VOC

P = atmospheric pressure

p_i = partial pressure of the VOC at the interface concentration and at the temperature of the solution

p_0 = vapor pressure of the VOC at the temperature of the system

r = coefficient of correlation ($S_{xy}/(S_{x2} \cdot S_{y2})^{0.5}$), where:
$S_{xy} = \Sigma(xy) - \{\Sigma(x) \cdot \Sigma(y)\}/n$
$S_{x2} = \Sigma(x^2) - \{\Sigma(x)\}^2/n$
$S_{y2} = \Sigma(y^2) - \{\Sigma(y)\}^2/n$
where: x is the independent variable and y is the dependent one; n is the number of data point pairs

V = characteristic velocity of the system

V_L = liquid velocity

V_{wind} = wind velocity above surface of the body of liquid

X_L = liquid phase mole fraction of the VOC in the bulk solution

X_i = liquid phase mole fraction of the VOC at the vapor-liquid interface

X_{sat} = VOC mole fraction in the liquid at saturation

Y_G = gas phase mole fraction of the VOC in the ambient air

Y_i = gas-phase mole fraction of the VOC at the vapor-liquid interface

$\beta_L, \beta_G, \beta'_G$ = dimensional constants relating the liquid phase and gas phase mass transfer coefficients to their respective diffusivities ((cm/sec)/(cm^2/sec)$^{0.67}$)

γ_∞ = liquid phase activity coefficient at infinite dilution of the aqueous VOC

μ = viscosity

ρ_L, ρ_G = liquid and gas densities, moles/cm^3

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APPENDIX

Error Estimation

Vaporization Rate Measurements

The precision of the vaporization rate measurement was determined in Gholson et al. [6]. It is estimated to be ±10% of the measurement.

Analytical Results

The variability of the concentration measurement was established. A summary of the VOC concentration ranges during the period of the investigation and of the variability of the measurements is given in Table 8. The results shown are for methanol, isopropanol, acetone and methyl ethyl ketone; no evaluation was made on the variability of the

TABLE 8. Relative Errors Contributed by the Analytical Methods & Sampling

VOS	ppm (wt) Levels in System	Relative Analytical Std. Dev.	Relative Over-all Std. Dev.
MEK	30–60	0.081	0.17
Acetone	30–50	0.068	0.27
iPOH	200–300	0.050	0.17
MeOH	400–600	0.039	0.15
Contribution to variability:		0.062	0.194

Notes for Table 8:

Contribution to variability = $\{[\Sigma(\text{standard deviation of each component}^2)]/n(=4)\}^{1/2}$

Relative Analytical Standard Deviation = Pooled Standard Deviation based on duplicate analyses of different samples/Average of Analytical Results for the VOC during that period

Relative Over-all Standard Deviation = Pooled Standard Deviation based on all samples taken from the equalization basin during the test period/Average of Analytical Results for that period

TABLE 9. Henry's Law Constants & Diffusivities of VOC's

VOC	Henry's Constant (atm)	Diff. Coeff. (in Air) (cm²/sec)	Diff. Coeff (in Water) (cm²/sec)
Toluene	405	0.086	9.67E-06
MEK	8.1	0.098	1.04E-05
MIBK	5.5	0.080	9.13E-06
Acetone	1.5	0.113	1.13E-05
iPOH	0.4	0.107	1.10E-05
MeOH	0.27	0.154	1.36E-05

methyl isobutyl ketone or toluene concentrations measurement.

Scatter in the measured concentrations arises from the variability in the analytical method and from the nonuniformity in sampling. The variability contributed by the analytical methods was estimated by analyzing each sample twice. That variability was expressed as a "relative analytical standard error," i.e., as the pooled standard deviation

of duplicate analytical measurements divided by the average concentration of that VOC. On the whole, the variability contributed by the analytical method amounted to 6%.

The combined scatter resulting from the sum of the analytical variability and the nonuniformity in sampling was estimated by analyzing different samples taken simultaneously from different parts of the basins. This total variability was expressed as a "relative over-all standard error," i.e. as the pooled standard deviation of the measured concentrations of a VOC divided by its average concentration. On the whole it amounted to 19%. Scatter is seen to be mostly a result of nonuniformity within the basins.

Errors in the Estimation of Henry's Law Constants

Henry's law constants were calculated for methanol, methyl ethyl ketone, acetone, methyl isobutyl ketone and isopropanol using the NRTL model with the Redlich-Kwong equation of state as provided by ASPEN.

It was assumed that the vapor-liquid equilibrium for each component within the system was the same as in two-component aqueous mixtures with no interactions between the components. For toluene, Henry's law constant was calculated based on its solubility in water at 25°C. It is expected that the standard errors are less than 10%. Henry's law constants at 25°C are listed in Table 9.

Errors in the Estimation of Diffusion Coefficients

Diffusion coefficients for all the solutes in water and for their vapors in air were calculated using the correlations of Reddy and Doraiswamy for the aqueous solutions and using the correlations of Wilke and Lee for diffusion in air [Reidetal, 7]. Errors in estimating these coefficients are expected to be less than 10%.

Diffusion coefficients estimated for the different VOC's in air and in water are listed in Table 9.

Over-all Error Estimation

The total standard error estimate resulting from combining analytical and sampling errors (approximately 19%), flux chamber measurement (10%) and physical property estimation (approximately 10% for the diffusivities and 10% for Henry's law constants) is then estimated to be about ±26%.

Field Evaluation of a Granular Activated Carbon Fluid-Bed Bioreactor for Treatment of Chlorobenzene in Groundwater

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Although granular activated carbon (GAC), fluidized-bed bioreactors have been used for treatment of groundwater containing readily biodegradable organic compounds, there is only limited experience with treatment of chlorinated organics found at many industrial sites. This paper describes a field evaluation of a GAC fluid-bed bioreactor operated at various chlorobenzene concentrations and organic loading rates over a 7-month period. Microorganisms used to seed the bioreactor were provided by activated sludge from the site, as well as indigenous chlorobenzene-degrading bacteria present in the groundwater. Removal efficiencies exceeding 99.99% were achieved at organic loading rates between 6 and 10 pounds of total oxygen demand (lb TOD) per 25 cubic feet per day. Influent chlorobenzene concentrations ranging from 100 to 170 ppm were consistently reduced to below the detection limit of 10 ppb. Economic evaluation indicates that groundwater treatment costs for the bioreactor were lower than other conventional technologies.

INTRODUCTION

Current practices to remediate contaminated groundwater beneath industrial sites frequently involve groundwater recovery and treatment. Installation of "pump-and-treat" systems has proven effective for achieving hydraulic containment of subsurface contamination, thereby eliminating off-site migration. Technologies frequently used for removal of contaminants from the groundwater include phase separation, air or steam-stripping and carbon adsorption. To avoid venting volatile organic compounds directly to the atmosphere, contaminants removed by air-stripping may be recovered on activated carbon or destroyed by thermal oxidation. Although biological processes have been used for many years for wastewater treatment, the application of biotechnology to groundwater treatment has often been limited by low concentrations of organic compounds, low microbial growth rates, and the inability to retain sufficient levels of active biomass in the reactors. However, recent

advances in the understanding of biofilm processes [1, 2], coupled with the development of fixed-film bioreactors have facilitated the application of biological processes to groundwater treatment [3, 4, 5].

Hickey and coworkers [5] have recently developed a granular activated carbon (GAC) fluidized-bed bioreactor system for treatment of contaminated groundwater. The technology offers several advantages over other commercially available bioreactors:

a) because pure oxygen is dissolved with the influent water, stripping of volatile organic compounds is essentially eliminated,

b) low strength wastes can be treated effectively because of the ability to maintain high biomass concentrations,

c) high removal efficiencies (low ppb effluents) can be achieved at short hydraulic residence times, and

d) fluidized-bed reactors are less prone to fouling or plugging than packed-bed systems.

Skid-mounted GAC fluid-bed bioreactors are commercially available and have been used for treatment of groundwater and process water containing readily biodegradable aromatic hydrocarbons, such as mixtures of benzene, toluene, ethylbenzene and xylene ([BTEX]; [5–10]). Economic evaluation suggests that biological treatment of BTEX-contaminated groundwater is cost-effective when compared with other conventional technologies such as air-stripping or carbon adsorption [10].

In contrast, substantial quantities of groundwater are contaminated with chlorinated organic compounds that have proven resistant to biodegradation. Extension of biological treatment technologies to such compounds will require that specialized microbial processes be discovered and refined. For example, until recently chlorinated benzenes were considered relatively resistant to biodegradation. Initial attempts to isolate bacteria capable of utilizing chlorobenzenes as sole carbon and energy sources frequently required extensive acclimation periods ranging from 6–12 months [11–13]. Over the past few years, bacteria capable of growth on a variety of mono, di- and trichlorobenzenes have been isolated and characterized [14–18]. One isolate, designated as *Pseudomonas* sp. strain JS150, was shown to have unique ability to biode-

grade a broad spectrum of chlorinated aromatic solvents alone or in combination with non-chlorinated homologs [18].

Extensive research on strain JS150 to determine the biochemical pathways and reaction mechanisms allowed for development of a pilot-scale bioreactor that proved highly effective in field trials [19]. During a demonstration conducted at Kelly Air Force Base, Texas, upflow fixed-film bioreactors were tested on groundwater containing a mixture of aromatic and chloroaromatic hydrocarbons. The reactors were capable of reducing the concentration of the groundwater contaminants from parts per million levels down to low parts per billion levels when operated at a hydraulic residence time of 40 minutes.

Microbiological analysis of the reactor during the field trial indicated that strain JS150 was eventually displaced by indigenous microorganisms present in the groundwater [20]. This observation raises the question of whether specialized bacterial strains are needed during startup of bioreactors for treatment of chlorinated aromatic compounds. To address this issue, Nishino et al. [20] have recently studied the distribution of chlorobenzene-degrading bacteria at contaminated sites. Competent bacteria were readily isolated from contaminated wells, whereas attempts to isolate chlorobenzene degraders from noncontaminated wells were unsuccessful. These results suggest that indigenous bacteria from contaminated sites rather than specialized laboratory strains could be used to seed bioreactors during startup. This conclusion is supported by the fact that activated sludge obtained from the site has been frequently used as the inoculum source for startup of GAC fluid-bed bioreactors. However, the use of specialized bacterial strains may be necessary in situations involving recent releases of chlorinated organics, or whenever specific degraders are not present in the indigenous microbial community.

The field trial described above [19] provided proof of concept, and bioremediation was recommended for treatment of chlorobenzene-contaminated groundwater at Kelly Air Force Base. However, additional studies were recommended to compare performance of fixed-film systems with other bioreactor configurations, and to determine treatment costs relative to other technologies.

The present study was conducted to examine the utility of GAC fluid-bed bioreactors for treatment of groundwater contaminated with chlorinated aromatic compounds. Objectives of the study were as follows:

a) evaluate potential sources of chlorobenzene-degrading bacteria to determine whether specialized strains or indigenous bacteria would be required during startup,
b) examine performance over a range of operating conditions and determine the effects of organic loading on effluent quality, and
c) compare costs of groundwater treatment using the GAC fluid-bed bioreactor with conventional groundwater treatment technologies.

MATERIALS AND METHODS

Microbial Enrichment

Microorganisms were enriched from samples of activated sludge and contaminated groundwater collected at the study site. Portions (10–50 mL) of the sludge or groundwater were transferred to 2-liter flasks containing 500 mL of mineral salts medium (pH 7.1; [21]). Chlorobenzene (99.99%; Aldrich Chemical Co., Milwaukee, WI) was supplied to the cultures as the sole carbon source using vapor bulbs as previously described [22]. The flasks were incubated on a rotary shaker at 200 rpm at ambient temperature (ca. 27°C). Samples were periodically removed from the cultures and analyzed for an increase in chloride concentration as described below. Microbial growth was also monitored by changes in optical density at 600 nm using a Bausch and Lomb Spectronic 20 spectrophotometer. The enrichment cultures were periodically transferred to fresh medium to eliminate non-chlorobenzene-degrading organisms. Individual isolates were obtained by plating on mineral salts agar [21] and incubation in a desiccator with chlorobenzene vapor at 25°C.

The utilization of chlorobenzene by the enrichment cultures was quantitatively measured by gas chromatographic analysis. Cells grown in mineral salts medium with chlorobenzene as the sole carbon source were harvested by centrifugation (6000 rpm, 30 min), and the cell pellet was suspended in fresh medium. Portions (1 mL) of this suspension were placed into serum bottles (160 mL) containing 50 mL of mineral salts broth. Cell densities in the reaction mixtures (as determined by plate counts) were in the range of $6-9 \times 10^6$ colony forming units per milliliter. To ensure maintenance of aerobic conditions, the bottles were purged with oxygen gas for 5 min. The cultures were then amended with various concentrations of chlorobenzene and immediately sealed with Teflon®-faced silicon rubber septa and aluminum crimp caps. Uninoculated control bottles were also prepared to characterize any abiotic losses. The serum bottles were incubated on a rotary shaker at 200 rpm at 25°C. Portions of the cultures were periodically removed and analyzed for chlorobenzene and chloride concentrations as described below.

Site Description

The field test was conducted at a Dow manufacturing facility where the groundwater has been previously shown to contain chlorobenzene (100 to 170 ppm), along with small amounts of aniline (< 5 ppm). To hydraulically control off-site migration, current remedial activities consist of groundwater recovery and treatment. Contaminated groundwater is recovered from a series of 25 wells and collected in a storage tank before treatment.

Volatile organic compounds are removed from the groundwater using a packed-tower air stripper associated with manufacturing operations at the site. Average groundwater and air flow rates to the stripper are 30 gpm and 300 scfm, respectively. Since the water receives additional biological treatment, chlorobenzene concentrations in the effluent are controlled to below a detection limit of 1 ppm. The overheads from the stripper are treated by thermal oxidation.

Before the study, a composite sample from the storage tank was analyzed for a number of conventional parameters. The water was slightly alkaline (pH 7.7) with total dissolved solids concentration of 2022 ppm. The predominant cations, sodium, calcium, and magnesium, were present at levels of 313, 220, and 52 ppm, respectively. Chloride (846 ppm) and bicarbonate (369 ppm) were the principal an-

ions detected. Only trace amounts (< 0.5 ppm) of inorganic nutrients such as nitrate and orthophosphate were present in the sample. The dissolved iron concentration of the groundwater was below the detection limit (< 0.05 ppm).

Bioreactor Design and Operation

The Envirex model 30 fluidized-bed bioreactor used for the field study included a skid-mounted column reactor and the supporting equipment. During the project, the GAC fluidized-bed reactor was installed parallel to the existing treatment system. The reactor column was 14 feet tall and 20 inches in diameter, and had a working volume of 210 gallons. The reactor was designed for a total fluidization flow (forward feed plus recycle) of 25 to 30 gpm to allow for 50% expansion of the bed. When the feed flow rate is 30 gpm, the hydraulic residence time within the reactor is approximately 7 minutes.

A simplified flow diagram of the system is shown in Figure 1. Influent water passes through a duplex basket strainer and is combined with the recycle flow from the reactor. Oxygen is then injected in-line and the water flows through an eductor where the hydraulic pressure differential enhances oxygen dissolution. Oxygen gas (purity 90–95%) is continuously generated and stored in a tank on the skid using a batch-type, pressure-swing-adsorption (PSA) system. As the water enters the bubble trap, a de-crease in the hydraulic velocity separates any undissolved gas which is reintroduced at the eductor. Periodically, a level control device in the bubble trap opens a valve and purges a small quantity of the gas bubble to the atmosphere via the recycle line. The water then enters the base of the reactor through a series of distribution nozzles and fluidizes the carbon bed. As microbial growth occurs in the reactor, the density of the carbon particles decreases, resulting in expansion of the bed. A mixer in the top of the reactor intercepts the bed at the 11-foot level and shears excess biomass from the carbon.

During startup, the reactor was loaded with 350 pounds of Calgon type MRX-P 10 × 30 granular activated carbon (Calgon Carbon Corp., Pittsburgh, PA). The unexpanded height of the carbon bed was 7 feet. The system was inoculated with 30 gallons of activated sludge obtained from the site wastewater treatment plant. The system was operated and maintained according to the operating discipline provided by the manufacturer [23].

Organic loading capacity of the bioreactor is a function of the oxygen transfer capacity of the system. Based on a working reactor volume of approximately 25 ft^3, the loading capacity for the model 30 ranges from 6 to 10 lb TOD per day [23]. Organic loading to the reactor was varied by adjusting the groundwater flow rate. Chlorobenzene loading in pounds per day was calculated using the equation:

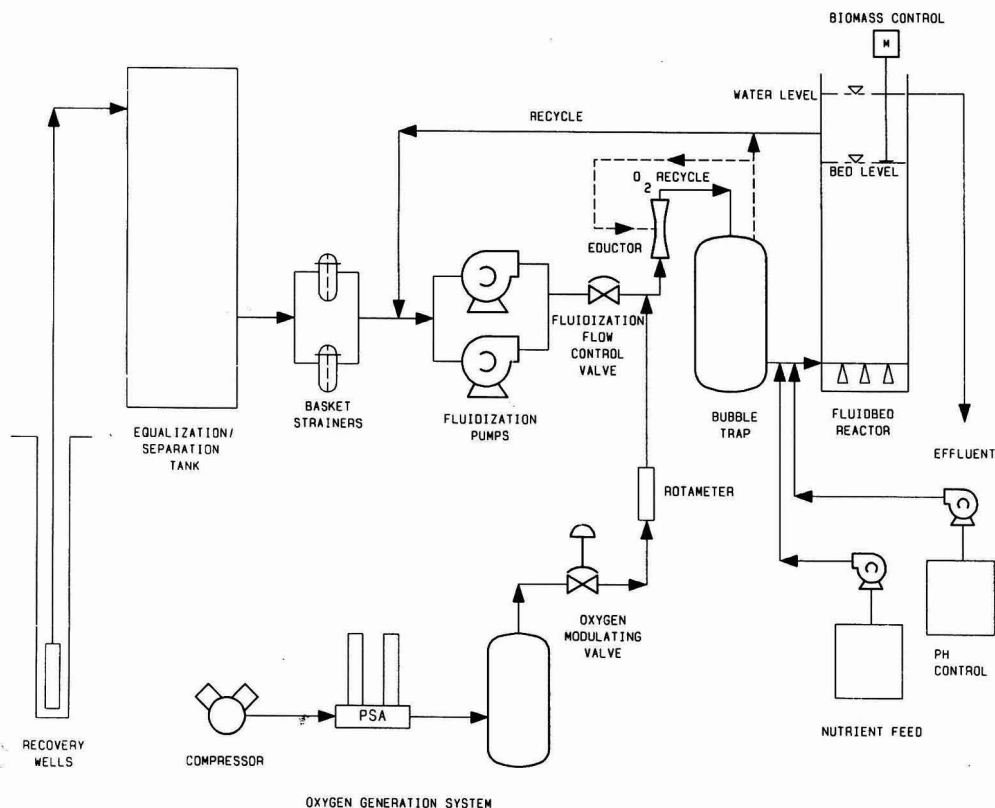$$LOAD \ (lb/day) = FLOW \ (gpm) * CONC \ (ppm) * 0.012$$

FIGURE 1   Process flow diagram for the Envirex fluidized-bed bioreactor.

Based on the theoretical oxygen demand for chlorobenzene (2 parts/part), the TOD loading was estimated by multiplying the chlorobenzene loading by a factor of 2.

Influent and effluent dissolved oxygen concentrations were continuously monitored using a Great Lakes Instruments model 697D/5340D dissolved oxygen analyzer system. The influent dissolved oxygen sensor was in-line prior to the reactor, while the effluent probe was located in the top of the reactor. The sensor probes were cleaned biweekly and the analyzer was calibrated monthly. Dissolved oxygen concentrations in the reactor were controlled by the effluent probe and a Powers model 535 process controller to maintain 2.5 ppm of oxygen in the reactor outlet. Oxygen consumption (in pounds per day) was routinely calculated on the basis of the recycle flow rate and the difference between the influent and effluent dissolved oxygen concentrations.

An inorganic nutrient solution was continuously supplied to the reactor based on the organic loading to satisfy a TOD:N:P ratio of 100:5:1 [24]. The solution was prepared by dissolving 9 pounds of Biotreatment Nutrient Mixture #36 (Milport Chemical Company, Milwaukee, WI) in 25 gallons of water. The mixture consisted of urea and diammonium phosphate (2:1). The flow rate of the nutrient pump was adjusted based on the organic loading according to vendor specifications. Inorganic nutrient concentrations in the effluent were monitored weekly throughout the investigation as described below; ammoniumion and orthophosphate concentrations ranged from 0.9 to 8.3 ppm, and 1.0 to 2.9 ppm, respectively, throughout the study period.

The influent and effluent pH levels were continuously monitored using Great Lakes Instruments model 672P pH analyzers and liquid crystal polymer-encapsulated sensors. Caustic (or acid) solution required to control the reactor pH was added to the system prior to the reactor inlet. The effluent controller was initially set to maintain the reactor pH in the range of pH 7.2 to 7.7. However, to avoid scaling due to calcium carbonate precipitation, the control set points were changed early in the study to maintain the reactor in the range of pH 6.6 and 6.8. Subsequent addition of caustic solution was not required to maintain the reactor pH at the desired level.

A variety of operating parameters were monitored throughout the field study. Instruments on the control panel monitored the groundwater, recycle and oxygen flow rates, reactor influent and effluent pH, dissolved oxygen levels, and temperatures. Water level in the bubble trap was monitored using a sight glass mounted on the outside of the tank. The carbon bed height was measured by lowering a small bucket sampler into the reactor and collecting samples at various known depths. A 1-pound weight was used periodically to conduct bed soundings to detect clumping of the carbon particles. Chlorobenzene concentrations were monitored in samples from the groundwater (feed) and reactor influent (feed + recycle) lines. Effluent chlorobenzene concentrations were measured in samples collected directly from the top of the reactor. The samples were collected in 40 mL vials containing 0.2 mL of dilute H_2SO_4 (1:1) as a stabilizer, and sealed with Teflon®-faced silicon rubber septa and screw caps. Effluent samples were also collected on a weekly basis for analysis of ammonia nitrogen, orthophosphate, total suspended solids and volatile suspended solids.

Analytical Methods

Chlorobenzene concentrations in aqueous samples (unfiltered) were routinely analyzed by direct injection using either a Varian model 3700 or a Hewlett-Packard model 5730A gas chromatograph equipped with a flame ionization detector. Separations were achieved with a column (120 cm × 3 mm i.d.) packed with Tenax® GC (60/80 or 80/100 mesh; Alltech Associates, Inc., Deerfield, IL) with a nitrogen carrier at a flow rate of 30 mL/min. The oven temperature was 190°C. Chlorobenzene concentrations were calculated from peak area measurements by comparison with an external standard prepared in water. The detector response was linear over the concentration range of interest (0–200 ppm), with a detection limit of approximately 0.5 ppm.

Aqueous samples containing low levels of chlorobenzene were also analyzed using a Hewlett-Packard model 19395A automated head-space sampler coupled to a model 5890A gas chromatograph equipped with a flame ionization detector. The head-space sampler was operated at the following conditions: sample temperature, 60°C; equilibration time, 240 min; valve/loop temperature, 65°C, pressurization time, 5 sec; injection loop fill time, 10 sec; and injection time, 36 sec. Head space samples were injected using a split ratio of 2:1 at an injector temperature of 200°C with a continuous septum purge of 5 mL/min. Chromatography was performed using a GSQ megabore capillary column (30 m × 0.53 mm i.d.; J&W Scientific, Folsom, CA). Compounds were eluted using a nitrogen carrier at a flow rate of 25 mL/min at a head pressure of 10 psi. The oven temperature was programmed to increase from 170°C to 215°C at a rate of 4°C/min. Output of the flame ionization detector was connected to a PE Nelson computer data system as above. The detector response was linear over the concentration range of interest (10 to 500 ppb) with a quantitation limit of 10 ppb.

Volatile emissions from the bioreactor column were periodically monitored using a TLV Bacharach organic vapor analyzer. The instrument was calibrated before use with a methane/air mixture. Chloride and ammonium ion concentrations were analyzed using Orion model 94-17 or model 95-12 ion selective electrodes, respectively, as described by the manufacturer. Ortho-phosphate was determined by the ascorbic acid method according to U.S. Environmental Protection Agency (EPA) method 365.2 [25]. Total and volatile suspended solids were determined by gravimetric analysis [26]. Additional groundwater samples were submitted to Midwest Laboratories, Omaha, NE for analysis of inorganic compounds.

RESULTS

Evaluation of Inoculum Sources

To determine if sources of chlorobenzene-degrading bacteria were readily available at the site, flasks containing mineral salts medium were inoculated with activated sludge or groundwater, and incubated with chlorobenzene as the sole carbon source. After 4 days, chlorobenzene degradation was indicated in the cultures by an increase in chloride concentration of the medium. Portions of the cultures were periodically subcultured to fresh media, and changes in chloride level and optical density were recorded. Rates
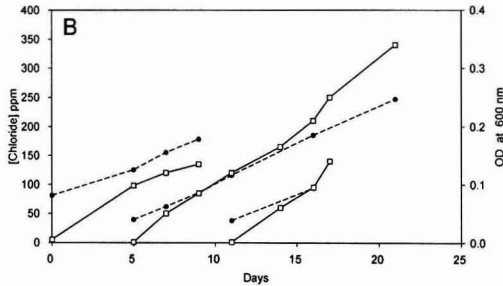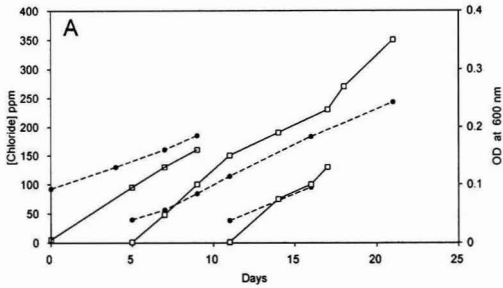
FIGURE 2 Enrichment of chlorobenzene degrading bacteria from (A) activated sludge and (B) groundwater samples. Changes in optical density (—) and chloride concentration (---) in the first, second and third subcultures.

FIGURE 3 Kinetics of chlorobenzene degradation by (A) activated sludge and (B) groundwater enrichment cultures. Chlorobenzene losses from non-inoculated controls were negligible (data not shown).

of chlorobenzene degradation (expressed as chloride released) were relatively constant in the cultures for each of three successive transfers (Figure 2). Degradation rates in activated sludge subcultures (11 to 14.1 mg chloride released per liter per day) were similar to rates observed in flasks containing the groundwater inoculum (10.8 and 12.9 mg Cl$^-$/L-day). The rates of microbial growth, as indicated by changes in optical density, were also similar in activated sludge and groundwater cultures. Considerable wall growth, evident in all cultures, suggested a preference for microbial attachment to surfaces.

Cells from each of the third subcultures were harvested and used as inocula for batch kinetic tests. Chlorobenzene was readily degraded in all cultures with the stoichiometric release of chloride (data not shown). The initial rates of chlorobenzene removal in cultures derived from groundwater were similar to those in cultures isolated from activated sludge (Figure 3). Chlorobenzene removal from the bottles was due to biodegradation, since negligible losses were observed in non-inoculated controls (data not shown).

Mineral salts agar plates inoculated from the enrichment cultures were incubated with chlorobenzene as the sole carbon source. After 1 week, white, cream or yellow colonies were observed. Based on colony morphology alone, at least 6 distinct types of chlorobenzene-degrading bacteria were present in cultures enriched from activated sludge, while 2 distinct types were isolated from the groundwater. These results suggested that a specialized inoculum would not be required during startup of the bioreactor, but that activated sludge from the site could be

employed. Because of the presence of chlorobenzene-degrading bacteria in the groundwater and by analogy with the results of Nishino et al. [20], it was anticipated that the activated sludge inoculum would eventually be displaced by the indigenous groundwater bacteria.

Bioreactor Startup and Operation

During startup, groundwater and fluidization flow rates were adjusted to 2 and 27 gpm, respectively, to preload the carbon with chlorobenzene. After 2 days, the reactor was inoculated with 30 gallons of activated sludge, the flow of groundwater to the reactor was temporarily stopped, nutrient addition was initiated, and the reactor was operated on internal recycle for 2 days. By the second day of operation in the recycle mode, evidence of biological activity in the reactor was indicated by a difference between the influent and effluent dissolved oxygen concentrations. Following startup, the groundwater feed was resumed and the bioreactor was operated for a total of 214 days.

Effects of Organic Loading on Treatment Efficiency

To examine the performance of the bioreactor over a range of operating conditions, the organic loading to the system was periodically changed by adjusting the groundwater feed rate. Performance data, divided on the basis of flow and organic loading are summarized in Table 1.

During the first 92 days, the reactor was operated for extended periods at average feed rates of 1.6, 2.8 and 4.0 gpm,

Days	Flow (gpm)	Recycle Flow (gpm)	Bed Height (ft)	Temp (°C)	TOD Loading (lb/Day)	Feed Cl-ben (ppm)	Influent Cl-ben (ppm)	Effluent Cl-ben (ppb)	Influent TOD (ppm)	D.O. Consumed (ppm)	DO/TOD (p/p)	Treatment Efficiency (% of Feed)
0–21	1.6	28.1	7.5	31.1	5.0	135.4	7.0	ND	14.0	13.8	0.99	> 99.5 or > 99.99
21–43	2.8	26.8	7.9	28.8	8.5	124.5	11.9	ND	23.8	22.2	0.93	> 99.5 or > 99.99
43–92	4.0	28.2	10.6	26.8	12.1	127.1	17.8	ND	35.6	27.9	0.78	> 99.5 or > 99.99
92–113	5.0	29.6	9.9	25.4	17.2	144.5	26.3	1087.0	52.6	22.2	0.42	99.25
113–130	3.5	29.5	9.0	24.1	10.2	123.2	12.3	506.7	24.5	24.4	1.00	99.59

corresponding to organic loadings of approximately 5.0, 8.5 and 12.1 lb TOD per day, respectively (Figure 4). Although the groundwater flow rates (feed) were relatively constant during each period, organic loading varied, due to changes in the groundwater composition. Since chlorobenzene concentrations in the groundwater ranged from 100 to 170 ppm (Figure 5), levels in the reactor influent (feed diluted with recycle) varied daily. Influent chlorobenzene concentrations for each of the three loadings were as follows:

a) days 0 to 21 = 7.0 ± 3.5 ppm (mean ± standard deviation)
b) days 21 to 43 = 11.9 ± 1.7 ppm
c) days 43 to 92 = 17.8 ± 3.6 ppm

In spite of the variation in loading, performance of the bioreactor was very stable, and effluent chlorobenzene concentrations (Figure 5) were generally below the detection limits. Chlorobenzene treatment efficiencies during the initial 13-week period typically exceeded 99.99%.

To examine the effects of extended operation at organic loading rates exceeding the design capacity, the flow rate to the reactor was increased on Day 92 from 4 to 5 gpm, thereby increasing the organic loading to an average of 17.2 lb TOD per day. Performance of the system gradually declined between Days 92 and 113 as indicated by oxygen limitations and increased levels of chlorobenzene in the effluent (Figure 5). However, the average treatment efficiency remained as high as 99%, as summarized in Table 1. Based on the mean concentrations of chlorobenzene in the groundwater (144.5 ppm) and the effluent (1.1 ppm), oxygen consumed in the reactor (22.2 mg/L), and the average influent (5 gpm) and recycle (29.6 gpm) flow rates, the mass balance for the system was as follows:

a) influent loading = 8.6 lb chlorobenzene/day
b) effluent losses = 0.1 lb chlorobenzene/day
c) TOD consumption = 7.9 lb oxygen consumed/day
= 3.9 lb chlorobenzene degraded/day

Based on the influent loading, about 45% of the chlorobenzene entering the reactor was removed by biodegradation, while 1% exited with the effluent. These results suggest that approximately 54% (4.6 lb chlorobenzene per day) of the material was removed by adsorption. Thus, the sorption capacity of the activated carbon allows the system to tolerate organic loadings in excess of the capacity with minor effect on performance.

On Day 113, the flow rate to the reactor was decreased to 3.5 gpm, thereby lowering the organic loading to 10 lb TOD/day (Table 1). Over the next 18 days, performance of the system appeared to return to normal. The carbon bed expanded from 8 to 10 feet in height, consistent with microbial growth in the system. Effluent chlorobenzene concentrations were typically below the detection limit, and treatment efficiencies generally exceeded 99.5%. The ratio of oxygen consumption to the influent oxygen demand ranged from 0.6 to as high as 3.1, with an average of 1.0. The fact that the oxygen consumption frequently exceeded the influent demand is consistent with biological regeneration of the activated carbon (i.e., biodegradation of adsorbed chlorobenzene).

Oxygen Consumption and Stoichiometry

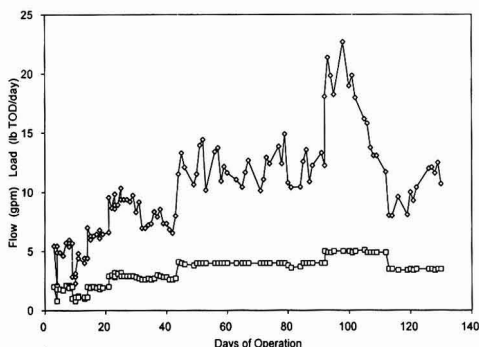Comparison of the difference between influent and effluent dissolved oxygen (DO) concentrations and the total

FIGURE 4 Reactor flow (□) and organic loading (◇) rates.
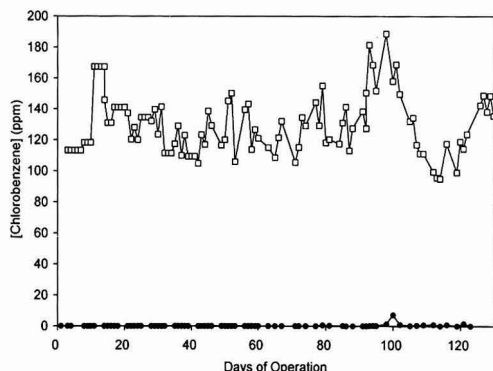

FIGURE 5 Chlorobenzene concentrations in the groundwater feed (□) and reactor effluent (●).

oxygen demand (TOD) of the influent stream (feed + recycle) was routinely used as an indication of bioreactor performance. When the reactor was operated near the design capacity (8.5 lb TOD/day; Days 21–43), oxygen consumption across the reactor generally agreed with the influent TOD (Figure 6). During this period, the average oxygen consumption and TOD values were 22.2 and 23.8 ppm, respectively (Table 1). The ratio of oxygen consumption to influent TOD (0.93 to 0.99) during the first 43 days of operation indicated that biodegradation was the principal removal mechanism.

At loading rates in excess of 10 lb TOD/day, the ratio of oxygen consumption to the influent TOD concentration decreased, indicating the inability of the oxygen delivery system to satisfy the oxygen demand of the influent stream. From Days 43 to 92, the difference between dissolved oxygen levels across the reactor ranged from 19 to 42 ppm, while the influent TOD concentrations were between 28 and 44 ppm. The average DO/TOD ratio of 0.78 for this period was consistent with a reactor loading of 12 lb TOD/day. From Days 92 to 113, when the loading to the reactor was 17 lb TOD/day, the DO/TOD ratio decreased to 0.43. These results provide additional evidence that when the design capacity of the reactor was exceeded, chlorobenzene removal was due to a combination of adsorption and biodegradation.

Growth and Biomass Yield

Biological growth was monitored throughout the study by measuring changes in the bed height (Figure 7) as well as the effluent concentrations of total and volatile suspended solids. Expansion of the bed occurs when the
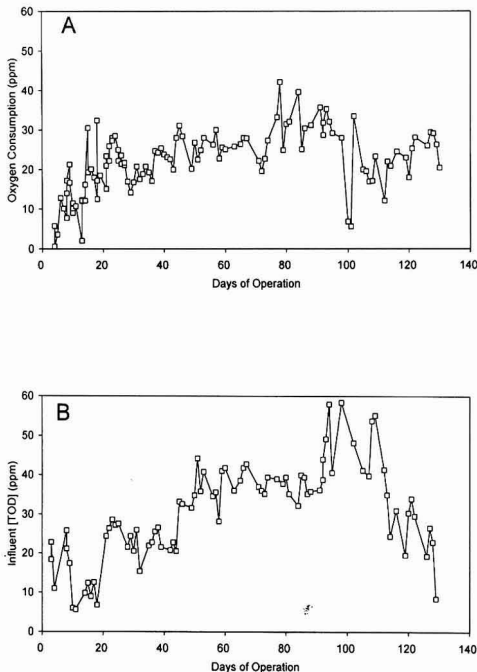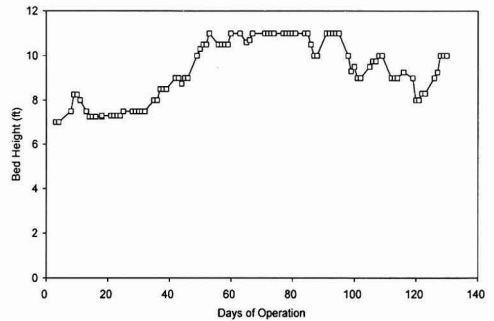
FIGURE 7 Changes in carbon bed height during operation of the reactor.

density of the carbon particles decreases as a result of increases in the biofilm thickness. Based on previous vendor experience, the rate of bed expansion varies with the organic carbon source and the growth rate of the microorganisms.

On Day 60, the bed height reached the 11-foot level and the biomass control system began operation, marking the beginning of "steady-state" conditions in the reactor. Effluent samples were collected weekly and analyzed for suspended solids. Total suspended solids levels ranged from 17 to 49 mg/L (mean = 34 mg/L) during the period from Day 60 to 92. Based on the average loss of 1.6 pounds of solids per day in the effluent, and a chlorobenzene loading of 6 lb/day, the cell yield was approximately 0.27.

Operation of the bioreactor at organic loading rates in excess of the design capacity (Days 92–113) resulted in clumping and packing of the carbon particles, and appeared to create channels within the fluidized bed. Frequent bed soundings with a large weight were required to break up the clumps. In some cases, a length of plastic pipe was used to apply sufficient agitation to break up large clumps in the bed. The increased extent and frequency of agitation of the bed may have resulted in significant losses of biomass from the system, which would account for the decline in the bed height noted from Days 98 to 113 (Figure 7). In addition, the loss of active biomass may account for the slight reduction in treatment efficiency observed during this period (99.25%).

Volatile Emissions

The air above the bioreactor was periodically monitored using an organic vapor analyzer to detect volatile losses of chlorobenzene from the system. Organic vapor concentrations ranged from trace to non-detectable levels, clearly indicating that biological treatment and sorption to the activated carbon were the principal removal mechanisms (data not shown).

Effects of Shock Loading

Prior to the shock-loading experiment, the system exhibited stable performance at an influent flow rate of 4 gpm (Table 1). On Day 63, the groundwater flow was increased to 8 gpm, thereby doubling the organic loading to about 22.4 lb TOD/day. The effluent chlorobenzene concentrations rapidly increased from nondetectable to levels as high

FIGURE 6 Comparison of (A) oxygen consumption and (B) influent total oxygen demand.

as 27.4 ppm during the shock (data not shown). Based on the mean groundwater (115.2 ppm) and effluent (26.6 ppm) chlorobenzene concentrations, oxygen consumption in the reactor (29.7 mg/L), and the average groundwater (8 gpm) and recycle (28.4 gpm) flow rates, the mass balance for the system was as follows:

a) groundwater loading = 11.2 lb chlorobenzene/day
b) effluent losses = 2.6 lb chlorobenzene/day
c) TOD consumption = 10.2 lb oxygen consumed/day
               = 5.1 lb chlorobenzene degraded/day

During the peak of the excursion, about 45% of the chlorobenzene entering the reactor was removed by biodegradation, while 23% exited the system with the effluent. Hence, it is likely that adsorption accounted for approximately 32% of the removal observed during the experiment.

Once the flow rate was restored to 4 gpm, the levels of chlorobenzene in the effluent rapidly declined. Within 2 hours, the effluent concentrations dropped to 12 ppb, and by Day 65, the levels were consistently below the detection limit of 10 ppb. To allow sufficient time for the reactor to recover prior to subsequent experiments, the system was operated until Day 92 at an influent flow rate of 4 gpm. Performance of the system during this period has been previously described.

ECONOMIC ANALYSIS

A series of scenarios were developed for comparison of the costs of groundwater treatment using the GAC fluid-bed bioreactor with a number of conventional technologies. A matrix of 4 case studies was developed on the basis of 2 flow rates and 2 groundwater concentrations as follows:

Case 1. 30 gpm flow and 30 ppm chlorobenzene
Case 2. 30 gpm flow and 150 ppm chlorobenzene
Case 3. 150 gpm flow and 30 ppm chlorobenzene
Case 4. 150 gpm flow and 150 ppm chlorobenzene

For each case, the capital, operating and maintenance costs for a number of groundwater treatment technologies were estimated. The treatment technologies included:

A. Liquid-phase activated carbon adsorption
B. Air stripping with vapor-phase carbon adsorption
C. Air stripping with thermal oxidation
D. GAC fluid-bed bioreactor

Each of the 4 treatment systems were functionally equivalent based on the ability to achieve an effluent discharge limit of 10 ppb.

Process Design

AspenPlus process simulation software was used to simulate the treatment process and determine the material and energy balance for each of the 16 technology and case study combinations. A general process schematic for each treatment technology is shown in Figures 1, 8 and 9.

Liquid-phase GAC adsorption was accomplished using 2 carbon beds in series (process schematic not shown). A third bed (off-line) was included in the design to accommodate changing spent carbon. The systems for treatment of 30 gpm flow rates consist of 5 foot tall by 5 foot diameter vessels filled with bulk carbon. The process design for
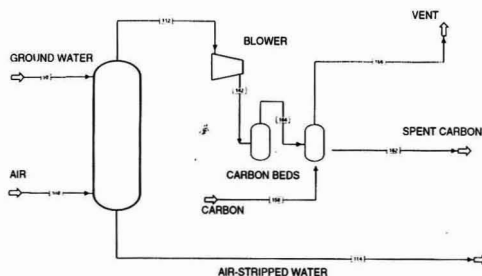
FIGURE 8   Process flow diagram for simulation of air stripping with vapor-phase carbon adsorption.

150 gpm flow rates required 6 foot tall by 6 ft diameter vessels. Carbon loading data was supplied by Calgon Carbon Corp. Loading capacities for influent concentrations of 30 and 150 ppm were 62.5 and 83.3 mg chlorobenzene per gram of carbon, respectively.

Figure 8 shows the basic design of the system used for air stripping with vapor-phase carbon treatment. In designing the air stripper, the vapor-liquid equilibrium for chlorobenzene was predicted to be non-ideal, so the UNI-QUAC activity coefficient equation was used [27]. Binary interaction constants were estimated from the chemical structure. The size of the stripper tower varied depending on the groundwater flow rate and chlorobenzene concentration. The diameter of the column ranged from 1.2 to 2.6 feet for groundwater flow rates of 30 and 150 gpm, respectively. Similarly, the height of the column ranged from 34 to 40 feet for influent chlorobenzene concentrations of 30 and 150 ppm, respectively. The height of the packing was estimated using the procedure described by Treybal for calculating the number of overall liquid-phase mass transfer units [28].

The vapor phase was treated using two carbon beds in series. Since humidity reduces adsorption capacity, an air blower was placed between the stripper and the carbon beds to raise the gas temperature by approximately 4°C, thereby lowering the relative humidity. For convenience, 55 gallon single-use canisters were used for the cases with lower chlorobenzene loadings (Cases 1B and 3B), whereas 8 foot tall by 8 foot diameter vessels filled with bulk carbon were used for cases with higher chlorobenzene concentrations (Cases 2B and 4B). Carbon loading data for vapor-phase treatment was supplied by Calgon Carbon Corp. At partial pressures of 0.0017 and 0.0087 psia, chlorobenzene loadings were reported to be 32 and 42% by weight, respectively. These values were reduced by 50% to account for humidity and by a factor of 0.85 to account
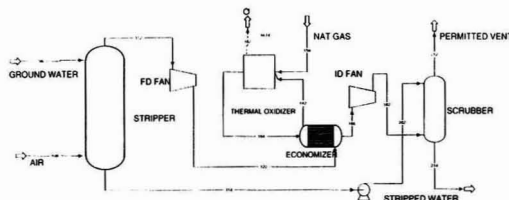
FIGURE 9   Process flow diagram for simulation of air stripping with thermal oxidation.

for efficiency. For influent chlorobenzene concentrations of 30 and 150 ppm, the vapor-phase loading capacities were 13.6 and 17.9% by weight, respectively.

As shown in Figure 9, chlorobenzene removed by air stripping was also treated using a thermal oxidizer. The system was designed with an economizer on the air side of the thermal oxidizer to recover heat, thereby minimizing fuel consumption. A forced draft fan pulls air through the stripper and pushes it into the thermal oxidizer. For safety, the concentration of combustible organics in the vapor phase from the stripper must be less than 25% of the lower explosive limit. An induced draft fan provides the required safe draft on the incinerator and pushes the flue gas through the air pollution control scrubber. The flue gas leaving the thermal oxidizer is scrubbed by contacting it with the treated groundwater.

The air stripper and the flue gas scrubber were designed using the same criteria as described above. The thermal oxidizer was sized using a factor of 200 standard cubic feet per minute of air per million BTU per hour and applying a safety factor of 30% to the air flow rate. The economizer was designed using an estimated heat transfer coefficient for 24 BTU per hour per square foot per degree-F and a safety factor of 50%.

Treated groundwater was used to scrub hydrogen chloride present in the flue gas to eliminate any additional hydraulic loading to the discharge. This would add approximately 10 ppm to 50 ppm of HCl to the discharge water depending on the initial chlorobenzene concentration. It was assumed that the groundwater would have sufficient buffering capacity to accommodate the acidity to avoid additional costs. When the alkalinity of the groundwater is low, additional neutralization may be required.

The design for the process simulation of the GAC fluid-bed bioreactor was based on the Envirex system (Figure 1). The height and diameter of the biological reactor were sized to achieve flux rates of 13 gpm per square foot and a hydraulic residence time of 7 minutes. For the process simulation, the diameter of the reactor vessel varied from 2.5 to 13 feet and the height from 16 to 21 feet depending on the flow rate and chlorobenzene concentration. The recycle flow rate was calculated from the greater of a) 30 gpm, b) 25% of the feed, or c) 2.9 gpm per pound of TOD per day. A minimum flow of 30 gpm through the bioreactor was assumed in order to fluidize the carbon bed. To buffer any potential step changes in the feed concentration, the system was designed with a minimum of 25% recycle. The organic loading capacity of the reactor was based on the solubility of oxygen in the reactor feed stream (32 ppm).

Basis of Economic Analysis

A number of factors are expected to influence the costs for treating groundwater with the various technologies. These include groundwater flow rate, nature and concentration of the contaminants, groundwater chemistry, physical site conditions, geographical location, size of the contaminant plume, and the treatment goals. In addition, the length of time that will be required to satisfactorily remove the contaminants adds considerable uncertainty to the remedial design. Because most pump-and-treat groundwater remediation projects are long term, the analysis assumes that the treatment project will last at least 10 years.

The economic analysis assumes that the contaminated groundwater will be pumped to the various treatment systems. Since the costs for installing extraction wells and delivery pipelines will be highly site dependent, they have not been considered. Discharge requirements are also expected to be site specific. For the present analysis, water treated by GAC adsorption or air stripping (coupled to either vapor-phase carbon adsorption or thermal oxidation) was assumed to be discharged to surface water at no cost. In contrast, due to the presence of suspended solids in the effluent from the GAC fluid-bed bioreactor, additional disposal costs may be incurred. For cases 1 and 3, effluent suspended solids concentrations in the range of 8 mg/L (based on 30 ppm chlorobenzene and a yield of 0.27) may be sufficiently low to permit direct discharge. In contrast, the levels of suspended solids resulting in cases 2 and 4 may warrant disposal of the effluent to a local publicly owned treatment works (POTW). Because of the uncertainty in discharge requirements, groundwater treatment costs for the bioreactor are presented with and without POTW disposal costs. For the present analysis, POTW charges were assumed to be $3.00 per 1000 gallons.

The following assumptions were also made for each case in this analysis:

- The groundwater contains low levels of iron and manganese and will not require pretreatment other than coarse filtration
- Utilities, including natural gas and electricity, are readily available at the site
- The treatment system will operate automatically
- A part-time technician will be required to operate the equipment, collect all required samples, and perform equipment maintenance and minor repairs
- One treated water sample and one untreated water sample will be collected daily to monitor system performance
- Treated and untreated water samples will be collected monthly and analyzed by an independent laboratory
- Costs of major repairs are included
- Taxes and insurance costs have not been included

Cost Categories

For the economic analysis, costs were allocated for the following categories: (1) project management, (2) permitting and regulatory requirements, (3) capitalized equipment, (4) startup, (5) demobilization, (6) labor costs for both operating staff and any necessary training, (7) consumables and supplies, including activated carbon and inorganic nutrients, (8) natural gas and electric power utilities, (9) analytical services, and (10) maintenance. Costs associated with each category are discussed below.

Project management costs include administration, treatability studies, and engineering costs. For this analysis the costs are estimated to be a one-time charge of $50,000. These costs are independent of the contaminant concentration and flow rate.

Permitting and regulatory costs are also assumed to be independent of the contaminant levels and flow rate. However, they will be highly dependent on whether treatment is performed at a Superfund or a RCRA corrective active site. For this analysis, these costs are estimated to be a one-time charge of $50,000.

Captialized equipment costs include purchasing and installing all treatment equipment. For this analysis, the costs of the equipment described in each process simulation were estimated using the Dow Factored Cost Estimation Program (data not shown). Capital costs also include instrumentation, computer control, and minimum shelter for the computer and any sensitive analytical equipment. When size permits, the process equipment will be pre-fabricated on skids and delivered to the site ready for start-up. Costs directly associated with equipment startup are included.

Expenses in the startup category include additional costs for developing a health and safety program for the site and one-time operator training costs. For this analysis, the startup costs are estimated to be $4000.

Demobilization costs include shut-down, disassembly and disposal of the equipment at a facility for hazardous waste. This analysis assumes that the equipment will have no salvage value at the end of the project. The costs were calculated based on a fixed charge of $7500 plus a variable 2% of the original capital cost. Since these costs will occur at the end of the project, they have been discounted to the present value.

Labor expenses are based on the assumption that each system will only require a part-time operator. Labor costs were estimated at $40,000 plus $3000 per year for annual health monitoring and safety training.

Consumables and supplies include personal protective equipment (e.g. steel-toed boots, full-face respirators and cartridges, gloves and safety glasses) that are predicted to cost $600 per year. Groundwater filtration costs of $50 per 300,000 gallons include purchase of new filter bags and associated disposal as hazardous waste. Miscellaneous expenses for oil, replacement gauges, pump seals and spare parts may also be incurred.

Activated carbon will be purchased either as 55-gallon single-use drums or in bulk. A single-use drum contains 200 pounds of carbon and costs $1300, which includes delivery and reprocessing. Single-use drums were used only for air stripping cases 1B and 3B. Bulk carbon was used for all other applications. The cost of bulk carbon for liquid-phase treatment was $1.25 per pound which includes delivery and reprocessing. Bulk carbon for vapor phase treatment was $1.75 per pound.

Nutrient costs were calculated from the stoichiometry of addition to satisfy a TOD:N:P ratio of 100:5:1. Based on the cost of the nutrient mixture, operating costs were estimated to be $0.13 per pound of TOD.

Utility costs include natural gas at $4.00 per thousand standard cubic feet (10^6 BTUs) and electricity at $0.08 per kilowatt-hour.

Analytical services costs include daily analysis of treated and untreated water samples. In addition, one sample per month will be analyzed at an independent laboratory. The independent laboratory will prepare monthly reports and yearly summaries.

Maintenance costs for each case were calculated as a percentage of the capitalized equipment costs. Maintenance costs are likely to be low during the first year of operation, higher in the last year, and highly variable. For this analysis, the costs were estimated to be an average of 5% of the capitalized equipment costs per year.

Treatment Costs

Cost estimates for each of the four treatment technologies for the four cases are presented in Tables 2 to 5. The costs were projected over a 10-year period. The total one-time costs are those that occur only once during the life of

TABLE 2. Economic Analysis of Liquid-Phase Carbon Adsorption

	Case 1A	Case 2A	Case 3A	Case 4A
Flow rate (gpm)	30	30	150	150
Chlorobenzene	30	150	30	150
Project management	50000	50000	50000	50000
Permitting and regulatory	50000	50000	50000	50000
Capital equipment	280000	280000	363000	363000
Startup	4000	4000	4000	4000
Demobilization	13100	13100	14760	14760
Total one-time costs	397100	397100	481760	481760
Labor				
Operating staff	40000	40000	40000	40000
Training	3000	3000	3000	3000
Consumables/supplies	3000	3000	12600	12600
Activated carbon	72000	270000	360000	1352000
Nutrients				
Utilities				
Natural gas				
Electrical	1432	1432	1432	1432
Analytical services	24000	24000	24000	24000
Maintenance	14000	14000	18150	18150
Total annual O&M costs	157432	355432	459182	1451182
Total yearly costs (10 yr)	197142	395142	507358	1499358
Cost ($) per 1000 gallons	13.69	27.44	7.05	20.82

	Case 1B	Case 2B	Case 3B	Case 4B
Flow rate (gpm)	30	30	150	150
Chlorobenzene (ppm)	30	150	30	150
Project management	50000	50000	50000	50000
Permitting and regulatory	50000	50000	50000	50000
Capital equipment	102000	190000	219000	640000
Startup	4000	4000	4000	4000
Demobilization	9540	11300	11880	20300
Total one-time costs	215540	305300	334880	764300
Labor				
Operating staff	40000	40000	40000	40000
Training	3000	3000	3000	3000
Consumables/supplies	3000	3000	12600	12600
Activated carbon	150800	144200	743600	722400
Nutrients				
Utilities				
Natural gas				
Electrical	1909	1909	3818	3818
Analytical services	24000	24000	24000	24000
Maintenance	5100	9500	10950	32000
Total annual O&M costs	227809	225609	837968	837818
Total yearly costs (10 yr)	249363	256139	871456	914248
Cost ($) per 1000 gallons	17.32	17.79	12.10	12.70

the project. The one-time costs were divided equally over the 10-year life of the project and added to the total yearly operating and maintenance (O&M) costs to calculate the total yearly costs. Treatment costs in dollars per 1000 gallons were calculated from the total yearly cost at the stated flow for 8000 hours per year. This value was selected to accommodate any down time that may be required for maintenance or repair of either the groundwater recov-

TABLE 4. Economic Analysis of Air Stripping with Thermal Oxidation

	Case 1C	Case 2C	Case 3C	Case 4C
Flow rate (gpm)	30	30	150	150
Chlorobenzene (ppm)	30	150	30	150
Project management	50000	50000	50000	50000
Permitting and regulatory	50000	50000	50000	50000
Capital equipment	724000	736000	2197000	2223000
Startup	4000	4000	4000	4000
Demobilization	21980	22220	51440	51960
Total one-time costs	849980	862220	2352440	2378960
Labor				
Operating staff	40000	40000	40000	40000
Training	3000	3000	3000	3000
Consumables/supplies	3000	3000	12600	12600
Activated carbon				
Nutrients				
Utilities				
Natural gas	1659	929	8394	4470
Electrical	5011	5011	16942	16942
Analytical services	24000	24000	24000	24000
Maintenance	36200	36800	109850	111150
Total annual O&M costs	112870	112740	214787	212162
Total yearly costs (10 yr)	197868	198962	450031	450058
Cost ($) per 1000 gallons	13.74	13.82	6.25	6.25

	Case 1D	Case 2D	Case 3D	Case 4D
Flow rate (gpm)	30	30	150	150
Chlorobenzene (ppm)	30	150	30‡	150
Project management	50000	50000	50000	50000
Permitting and regulatory	50000	50000	50000	50000
Capital equipment	143000	284000	284000	607000
Startup	4000	4000	4000	4000
Demobilization	10360	13180	13180	19640
Total one-time costs	257360	401180	401180	730640
Labor				
Operating staff	40000	40000	40000	40000
Training	3000	3000	3000	3000
Consumables/supplies	3000	3000	12600	12600
Activated carbon				
Nutrients	936	4680	4680	23400
Utilities				
Natural gas				
Electrical	4295	14795	14795	48202
Analytical services	24000	24000	24000	24000
Maintenance	7150	14200	14200	30350
Total annual O&M costs	82381	103675	113275	181552
Total yearly costs (10 yr)	108117	143793	153393	254616
Cost ($) per 1000 gallons	7.51	9.99	2.13	3.54
With POTW disposal costs		12.99		6.54

ery or treatment systems. All costs are presented in 1994 dollars and are considered to be order-of-magnitude estimates.

Comparison of the data presented in Tables 2 through 5 indicates that for a given flow rate, the cost of groundwater treatment (in $/1000 gallons) generally increases as the concentration of the contaminants increases. However, economy of scale differences are also readily apparent, since unit treatment costs for the higher flow rates were generally less than those for lower flows.

Of the four technologies examined, the costs for groundwater treatment using the GAC fluid-bed bioreactor were generally lower as compared to the more conventional methods. Bioreactor costs ranged from $2.00 to $13.00 per 1000 gallons, and were highly dependent on the influent concentration, flow rate and potential POTW disposal charges. Groundwater treatment by liquid-phase carbon adsorption was the most expensive ($7.00 to $27.00 per 1000 gallons), primarily because of the costs for replacement and disposal of the spent carbon. Air stripping with vapor-phase adsorption was more expensive than air stripping coupled to thermal oxidation. At the higher flow rates, the costs for the latter are estimated to be about half of those for systems with vapor-phase carbon treatment.

Additional differences between the four technologies are evident from a comparison of capital and yearly operating and maintenance costs. Capital costs for liquid-phase adsorption and air stripping with vapor-phase adsorption were among the lowest, ranging from $280,000 to $363,000 and from $102,000 to $640,000, respectively. In contrast, yearly operating and maintenance costs for these two methods were very high, ranging from $150,000 to $1,500,000, with the bulk of the expense associated with carbon replacement. Capital costs for GAC fluid-bed bioreactor were also relatively low, ranging from $143,000 to $607,000. Note that while these capital estimates were derived from the process simulation and the individual component costs, they are comparable to the costs of commercially available skid mounted bioreactors. Of the technologies examined, capital costs for the air stripper and thermal oxidizer system were the most expensive, ranging from $720,000 to $2,200,000. However, the air stripper/thermal oxidizer and the GAC fluid-bed bioreactor both had lower yearly operating and maintenance costs.

DISCUSSION

Our results are consistent with previous reports describing the performance of GAC fluid-bed bioreactors during full-scale evaluations. Removal efficiencies exceeding 99% have been frequently reported for treatment of groundwater containing mixtures of readily biodegradable aromatic hydrocarbons resulting from fuel spills [7-9, 29]. Recently, Eckel et al. [30] described similar performance for the biological treatment of groundwater containing a complex mixture of volatile and semivolatile organic compounds which included several chloroanilines and chloronitrobenzenes. These results clearly demonstrate the effectiveness of GAC fluid-bed bioreactors and expand their application for treatment of a wide range of organic compounds, including chlorinated hydrocarbons.

The maximum organic loading capacity of the bioreactor was a function of the ability to provide sufficient oxygen

for biodegradation. Furthermore, the ability to satisfy the oxygen demand was shown to have the greatest effect on maintaining high treatment efficiencies. With the current design, the capacity to provide dissolved oxygen is controlled by the purity of oxygen gas produced by the oxygen generator and the transfer efficiency of the injection, bubble trap and eductor system. According to the manufacturer, the capacity of the current 25 ft^3 reactor is in the range of 6 to 10 lb O_2 per day. Although observations during the present study suggested that as high as 15 lb O_2 per day could be delivered, the majority of the values fell below 10, consistent with manufacturers specifications. Recently, Envirex has developed a new pressurized bubble contactor which reportedly can achieve significantly higher oxygen transfer efficiencies. Preliminary indications suggest that with the new design, the loading capacity of the bioreactor could be increased by 50 to 100%.

When the bioreactor was operated at organic loading rates in excess of the design capacity, adsorption also appeared to play a role in maintaining high treatment efficiencies. Adsorption capacity expended during operation at the higher loading was biologically regenerated as evident by the fact that oxygen consumption frequently exceeded the influent TOD concentration when the loading was decreased from 17 to 10 lb TOD/day. The adsorption capacity of the system also served to dampen the effects of loading changes caused by moderate variations in the groundwater composition. In addition, treatment efficiencies did not appear to be affected by step changes in groundwater flow rate, which increased loading to the reactor by 1.4-fold increments (e.g., 8.5 to 12 lb TOD/day). In contrast, the adsorption capacity of the carbon was less effective in dampening the effects of a major shock load. When loading to the reactor was doubled from 12 to 24 lb TOD per day, effluent chlorobenzene concentrations rapidly increased. However, the effects were temporary, since the effluent concentrations rapidly declined when the loading was restored to previous levels.

Of the various types of fixed-film reactors, the GAC fluid-bed reactor offers several advantages over packed-bed units [10]. With the latter, as growth occurs the system may eventually plug as the support media becomes packed with biomass. Plugging may also result due to precipitation and accumulation of calcium carbonate or ferric iron. Furthermore, the fluid-bed process provides substantially larger surface area for biofilm growth as compared to packed-bed units, which is consistent with the fact that high treatment efficiencies can be achieved at substantially shorter residence times. In the present study, chlorobenzene concentrations were reduced to below the detection limit at hydraulic residence times in the range of 50 to 130 minutes. It is important to note however, that the reactor was undersized with respect to the organic loading of the feed stream, and dilution with the recycle flow was necessary to maintain bed fluidization and decrease the loading to a range within the design capacity. When the organic concentration of the feed stream is within a range that allows once through flow, high treatment efficiencies can be achieved at hydraulic residence times as low as 7 minutes.

Based on the results of the present study, chlorinated aromatic hydrocarbons can be effectively treated using GAC fluid-bed bioreactors. Although for many years, chlorinated organic compounds were considered to be relatively resistant to biodegradation, recent reports suggest that many can indeed support microbial growth. In addition to mono and dichlorinated benzenes, a number of volatile chlorinated aliphatic compounds, including methylene chloride, ethylene dichloride, vinyl chloride and 2-chloroethylvinylether have been shown to serve as carbon sources for growth [31–34]. Several of these have been shown to be effectively removed in laboratory-, or pilot-scale biological treatment systems [35–37]. In view of the many advantages of commercially available GAC fluid-bed bioreactors, particularly the in-line dissolution of pure oxygen which eliminates losses due to volatilization, biological treatment of groundwater or process waters containing volatile chlorinated compounds represents an attractive and cost-effective alternative to conventional treatment technologies.

In contrast, contaminated groundwaters can contain chlorinated organic compounds that do not readily support microbial growth. Extension of this technology for treatment of such compounds will require that additional specialized biological processes be discovered and refined. Many chlorinated compounds have been shown to be aerobically biodegraded by the process of co-oxidation [38]. In such systems, oxidation of nongrowth substrates occurs fortuitously while the microorganisms are grown at the expense of an alternate carbon and energy source. Recent work on the development of reactor systems based on the principles of co-oxidation of chlorinated aliphatic hydrocarbons in the presence of methane or certain aromatic compounds, appears to hold some promise [39–42]. Alternatively, since many chlorinated hydrocarbons are known to undergo reductive dehalogenation to lower chlorinated homologs under anaerobic conditions [43], effective treatment may be achieved by combinations of anaerobic followed by aerobic biodegradation [44].

In conclusion, GAC fluid-bed bioreactors are highly effective for the treatment of groundwater and process wastewaters containing a wide variety of chlorinated and nonchlorinated organic compounds capable of supporting microbial growth. The systems have been shown to achieve high treatment efficiencies (> 99.99%) and reliable performance when operated according to an established operating discipline. Economic evaluation suggested that groundwater treatment costs for the bioreactor were lower than several conventional water treatment technologies.

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The First Full-Scale Soil Washing Project in the USA

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In mid-1992, Geraghty & Miller, Inc. and Heidemij Realisatie of The Netherlands incorporated the joint venture of Alternative Remedial Technologies, Inc. (ART) to implement soil washing projects in the United States. The venture was based upon Heidemij's successful commercial soil washing operations in The Netherlands over the past decade. The first project contracted under this arrangement was the King of Prussia (KOP) Technical Corporation Superfund site, located in Camden County, New Jersey. This paper presents the details of activities at this site and operation of the full-scale soil washing facility. At the KOP site approximately 20,000 tons (20,320 metric) of soil contaminated with copper, chromium and nickel were remediated. The KOP plant is rated at 25 (25.4 metric) tons per hour (tph) and is configured in a way that allows flexible treatment capabilities for sites with metals, polynuclear aromatics, pesticides, and radioactive contamination.

INTRODUCTION

In 1992 ART was selected to perform soil washing operations at the KOP site in Winslow Township, Camden County, New Jersey. ART is a joint venture company of Geraghty & Miller, Inc. (USA) and Heidemij Realisatie (The Netherlands). Heidemij has successfully operated soil washing equipment on full-scale projects in The Netherlands for over ten years and is supporting ART in bringing this innovative technology to the United States. This was the first full-scale soil washing operation in the United States, and the first cleanup of a Superfund site through the use of this innovative technology.

Site Background

The KOP site is approximately ten acres and is located on Piney Hollow Road in Winslow Township, New Jersey, within the Pinelands National Reserve (Figure 1). It is also adjacent to the State of New Jersey's Winslow Wildlife Refuge. The Great Egg Harbor River is located about 1,000 feet (304.8 m) southwest and downgradient of the site.

The KOP Technical Corporation purchased the site from Winslow Township in 1970 for the purpose of processing and recycling hazardous wastes. Six lagoons were used to process liquid and industrial waste with the intention of converting the materials into a marketable product. Sometime between 1973 and 1975 operations ceased and the site was abandoned. In 1976, Winslow Township foreclosed on the property and the site fell under the ownership of the

United States Environmental Protection Agency (USEPA) Region II. The site consisted of six lagoons which were utilized for industrial waste processing. Three of the lagoons could still be visually identified and a fourth was marked by a slight depression.

USEPA conducted a Remedial Investigation (RI) of the site between 1987 and 1989. High levels of metals contamination, specifically, chromium, copper and nickel, were found in lagoon sludges and in soils surrounding the lagoons as well as in the swale. Concentrations of volatile organic compounds (VOCs) were found in an area containing buried drums. Metals and VOCs were found in the groundwater beneath the site, extending toward the Great Egg Harbor River. During the RI, buried plastic containers (carboys) and surrounding soils with visible contamination, located west of the lagoons, were excavated and disposed off-site. Based on the results of the RI, USEPA conducted a Feasibility Study (FS). The FS identified and evaluated the most appropriate technical approaches for addressing contamination at the site. Based on the results of the RI/FS, USEPA issued a Record of Decision (ROD) for the site in September of 1990 which required specific actions for remediation of soils and groundwater. Soil washing was specified as the cleanup technology to be used for remediation of the soils. In April 1991, USEPA issued a Unilateral Administrative Order (Order) to the Potentially Responsible Parties (PRPs), requiring them to fulfill the requirements of the ROD.

Site Activities

Since the ROD was issued, extensive progress has been made toward total remediation of the site. During 1990 and 1991, on-site tankers and approximately 200 buried drums were removed. These materials were transported to an off-site disposal facility. An extensive sampling program was conducted in 1992, the purpose of which was to further delineate soil and groundwater contamination identified in the ROD. In addition, surface, sediment, and fish tissue samples were collected to assess the impact of site contamination on the Great Egg Harbor River. In 1995, following a Risk Assessment for the former Buried Drum Area VOC-contaminated soils, the USEPA proposed a No Further Action remedy. Soil remediation activities began in June 1993 and were completed in October 1993. Following the completion of soil remediation, a Habitat Restoration Plan was implemented and a ground water remediation plant was constructed on the pad which formerly held the soil washing plant.
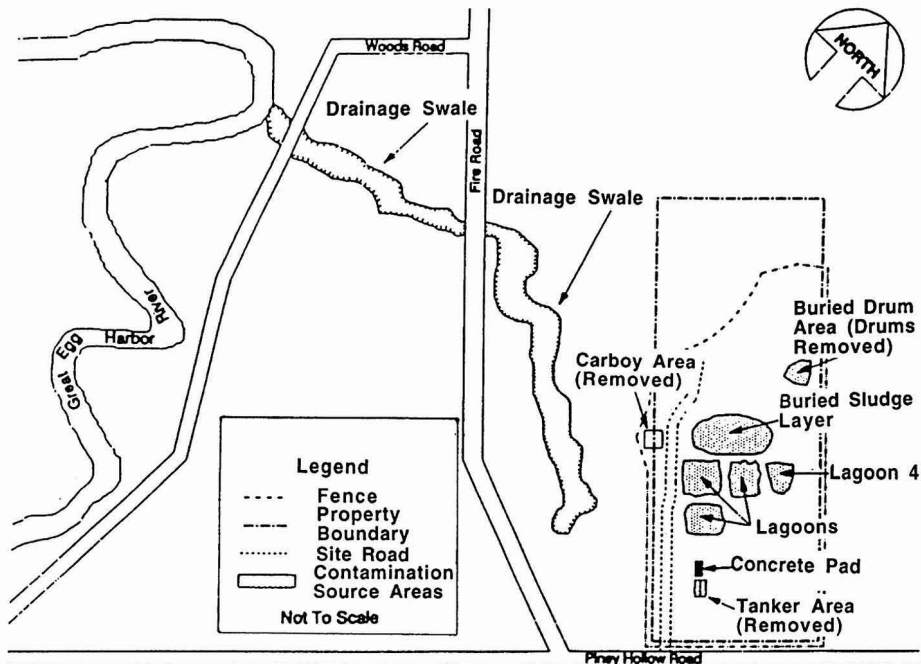
FIGURE 1   Site map.

ART Soil Washing Activities

The first step taken in designing the soil washing plant to clean on-site soils (e.g., lagoon sludges, soils adjacent to the lagoons, and sediment in the swale) was to conduct treatability and bench-scale studies to define the contaminant/particle-size relationship and construct the particle-size curve (Figure 2). Those studies were successfully completed in early 1992. It was then proposed to perform a "Demonstration Run" on actual KOP site materials at the full-scale Heidemij plant located in Moerdijk, The Netherlands. About 200 (203.2 metric) tons of contaminated soils and sludges were shipped from the KOP site to Moerdijk, where a one-day run was performed simulating the operations which would perform the soil washing at the KOP site. The demonstration run successfully treated the KOP soils and sludges to the cleanup levels specified in the ROD. Post-run analyses showed that actual levels well below
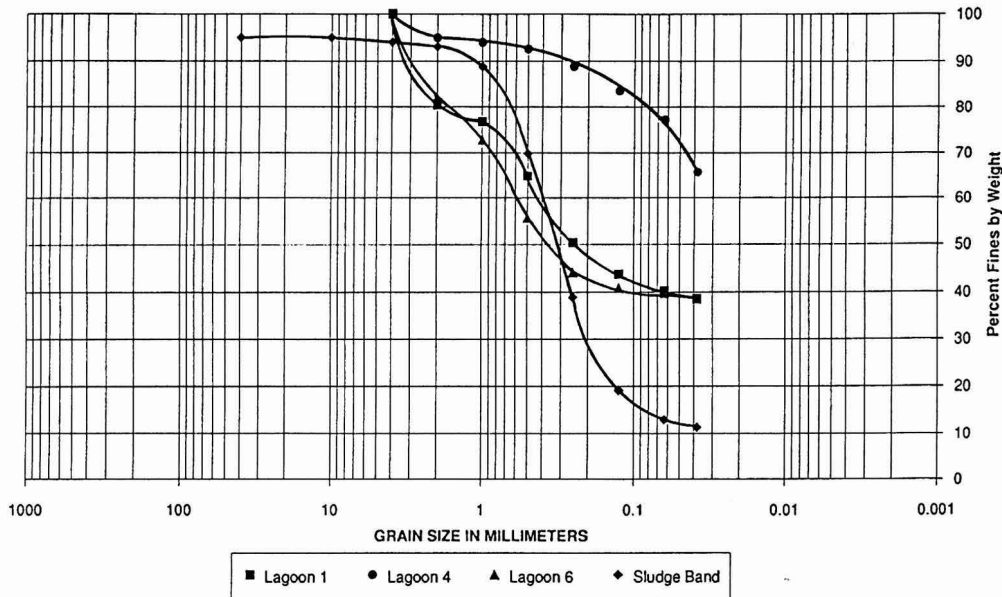
FIGURE 2   Particle size distribution curves.

the ROD-specified standards were achieved during the performance of the demonstration run.

Based on the success of this run, the remedial design schedule was "fast-tracked" and one year was reduced from the schedule. The firm of SALA International was contracted by ART to manufacture the soil washing plant and delivery of the plant to the site was completed in May 1993.

THE PROCESS

The plant consists of four major sub-systems:

- Screening
- Separation
- Froth Flotation
- Sludge Management

Each of these sub-systems is now described.

Screening

A working pile is excavated in the field. The working pile must first be screened to remove the gross oversize fraction. This will normally be accomplished using a hopper mounted with a vibrating grizzly. If hopper blockage results, it may be necessary to substitute a Kombi screen or Trommel screen to provide a more uninterrupted step. Gross oversize material is periodically removed from the hopper area and staged for recycling. The "fall through," or the material < 8" (20.34 cm), is conveyed to the next mechanical screening unit, which will generally consist of a double-decked vibrating screen with stacking conveyors. The double-decked screen will have two flow paths: 1) an oversize material that is greater than 2" (5.08 cm), and 2) a fall-through that is directed by conveyor to the wet screening unit. Wet screening is applied to the stream of soil < 2" (5.08 cm). High-pressure water nozzles attack the influent stream, breaking up small clods, dropping out pea-sized gravel and forming the slurry that is now pumped to the separation sub-system.

Separation

The heart of the soil wash system, and the area where extensive experience has been developed is the creative use of hydrocyclones. Conceptually, the use of hydrocyclones is simple: the influent soil/water slurry is pumped to the hydrocyclone and the slurry enters tangentially. In the hydrocyclone, open to atmospheric pressure, the coarse-grained sands are spun out of the bottom, while the fine-grained materials and water are ejected from the top of the unit.

Several details need to be pointed out regarding the special use of the hydrocyclones in this system. First, the hydrocyclones have field-adjustable cone and barrel components such that the "cut-point" interface between coarse and fine-grained materials can be modified to be consistent with treatment needs. This is extremely important in achieving the smallest possible volume of sludge cake requiring off-site disposal. Secondly, the hydrocyclones can be arranged in many flow-path configurations depending upon the interface needs and the goal of minimizing coarse-grained carryover into the fines.

Depending upon the soil to be treated, it may also be beneficial to utilize gravity separators on either or both of the coarse/fine fractions. Typical applications might include the removal of a floating organic layer, or at the other end of the density spectrum, dropping lead out from the soil-treatment stream.

Froth Flotation

The underflow from the hydrocyclones contains the coarse-grained materials. When treatment is required for this fraction, it is accomplished using proven air flotation treatment units. The first important decision that must be made in this sub-system is the selection of a surfactant. The selection, made from scores of alternatives, has one objective: the surfactant, when contacted properly with the contaminant/soil mass, reduces the surface tension binding the contaminant to the sand and allows the contaminants to "float" into a froth which is then removed from the surface of the air flotation tank. The selection of the appropriate surfactant is made during the treatability study at the bench-scale level.

The air-flotation tank is a long, rectangular tank that is mixed with the use of mechanical aerators and diffused air. Retention time is typically about 30 minutes, but can be adjusted on the treatment unit. The flotation units require operator experience to obtain optimal performance. Primary control parameters are surfactant dosing, slurry flow rate, air flow rate, and the height of the overflow weir.

Two streams, the overflow froth, and the underflow sand, are the effluents from this treatment unit. The froth is concentrated and usually directed to the sludge management belt filter press where it is dewatered into a 50–60% solids cake. If, however, the contaminants from the coarse and fine-grained fractions are not compatible, then it may not be wise to send the froth to the filter press, but to manage it separately. The underflow from the flotation unit (the sand) is now directed to sand dewatering screens—the dry sand represents the "clean" material that will be reused, the water is recycled back to the wet screening section.

Sludge Management

The overflow from the hydrocyclone, consisting of fine-grained materials and water is now pumped to the sludge management sub-system. As mentioned earlier, the fines represent the most difficult fraction to treat, as a result of complex binding and attachment dynamics and mechanisms. If the distribution of fines to coarse is favorable, it is feasible to simply treat the fines in a manner similar to a wastewater sludge by polymer addition, sedimentation, thickening, and dewatering. If the fines/coarse ratio is not that favorable, it may be necessary to consider more sophisticated treatment. Of course, this upgraded treatment will depend upon the contaminants of concern, but it may include biological degradation or metals extraction.

In the primary case (simple treatment), the hydrocyclone overflow is pumped to the sedimentation area, currently consisting of banked Lamella clarifiers. An appropriate polymer is selected in lab jar testing, and is dosed prior to introduction to the Lamella. The clarified solids are directed to a sludge thickener, while the water overflow is returned to the wet screening area for reuse. The thickened solids are then pumped to a pressurized belt filter press. This unit is one of the most important in the entire process in terms of selection. The 15–20% solids influent is

converted into a 50–60% dry solids filter cake. This cake contains the target contaminants and therefore must be managed by disposal at a properly permitted off-site disposal facility, depending upon the specific contaminants and their status in regard to current land bans.

Residuals Management

An important decision that must be made in selecting a soil washing system is the manner in which the residuals from the treatment system will be managed. There are three primary residuals to be handled:

- The Oversize and Gross Oversize Material
- The Clean Coarse-Grained Material (The Sand)
- The Fine-Grained Material (The Sludge Cake)

For the oversize material, efforts will be taken to reuse the material. Wood and wood products can be shredded, in many areas this material can be used as a supplemental fuel in co-generation facilities. Steel scrap can be sold to mini-mills, and concrete rubble can be crushed for use as aggregate in concrete production.

The clean sand can be used as select backfill, and can usually be returned directly to the area of excavation. If the site conditions do not require the area of excavation to be regraded, the clean material can be used as a construction grade material for other development uses onsite, such as roadways or concrete. In some states, with California leading the way, this "clean" material can be sold for off-site uses after meeting certain criteria.

The fine-grained materials, where the contaminants reside, will require disposal off-site, usually at a RCRA Treatment Storage and Disposal Facility (TSDF). When the job is initially scoped we will make solid determinations regarding the type of disposal or treatment facility that will be required for the specific fine-grained residuals from the site. The choice of treatment facilities will usually be limited to a hazardous waste landfill or a fixed-base incinerator. This decision will hinge upon the status of the specific waste(s) with regard to the Land Disposal Restrictions (LDRs), commonly known as the land bans.

SITE REMEDIAL ACTIONS

During March 1993, the remedial action for soils began with the excavation and off-site disposal of Lagoon 4. The treatability studies conducted early in 1992 determined that Lagoon 4 contained sludge only and was not amenable to on-site treatment.

Following delivery and construction of the soil washing plant at the site, a pilot run was conducted on 1,000 tons (1,016 metric) of contaminated soils excavated from the site. The pilot run was successful, and again cleanup levels well below the ROD-specified standards were met.

Full-scale soil washing operations began on June 28, 1993 and were completed on October 10, 1993. During the operation of the soil washing facility, the cleaned soils were

returned to the site as backfill. The contaminated fraction was disposed at an off-site facility. At the completion of the soil washing phase, the facility was disassembled and removed from the site. Revegetation has been completed and the site restored to its natural condition. The entire project treated 19,507 tons with an achieved volume reduction of 83%.

The project was performed with full-time EPA oversight, in accordance with the approved Site Operations Plan (SOP). Process and product analytical work was split between the use of on-site X-ray Fluorescence (XRF) and off-site Contract Laboratory Procedure (CLP) analysis. The overall results for the project were as follows:

Contaminant	Feed Range (mg/kg)	Avg. Concentration (mg/kg)		
		ROD Std.	Clean Product	Residual
Chromium	500–5,500	483	73	4,700
Nickel	300–3,500	1,935	25	2,300
Copper	800–8,500	3,571	110	5,900

LESSONS LEARNED

As the first full-scale soil washing remedial action performed in the United States, it is important to review this project so that future projects may benefit from its successful implementation. Key components to be discussed are:

- It is possible to establish a cooperative, working team among the USEPA, the state agency, the PRP Committee, the consultant, and the contractor.
- Treatability studies should focus on the products of the process, specifically the oversize, the sand, and the sludge cake, and not on intermediate products.
- The demonstration of a full-scale process capability prior to the site implementation was extremely helpful.
- Since there are many definitions of "soil washing," the project team should clearly understand the technology details for implementation on a specific site.
- Define the sampling and analysis program before the process is utilized in the field.
- Recognize that no site can ever be fully characterized prior to site construction. Therefore, plan for flexibility in the field program, particularly in the excavation phase.
- Prepare for, and invest in, the use of field analytical to control the process and products.
- Establish objectivity in the development of data and require the team to work together to solve site problems.

Soil washing is now a proven technology in Europe and is widely applied on a broad range of contaminated soil projects. While still viewed as an "innovative technology" in the U.S., its use and applicability make it a natural choice for many of our remedial needs.

Scale-Up and Economic Analysis for the Design of Super-critical Fluid Extraction Equipment for Remediation of Soil

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The magnitude of the contaminated site clean-up in the United States indicates the need for more effective, less costly remediation technologies. Supercritical Fluid Extraction (SFE) using carbon dioxide (CO_2) as a super-critical fluid is a possible alternative technology for remediation of soils contaminated with volatile organic compounds. The feasibility of this process is mainly dependent on two factors: the extent and extraction rate of heavy molecular weight organic compounds from soil by supercritical carbon dioxide ($SC\text{-}CO_2$). This paper presents results of a bench-scale study for remediation of soils contaminated with naphthalene and 1,2,4 trimethyl benzene as a function of the flow rate (Q_{CO_2}) and supercritical fluid density (ρ_{CO_2}). These data are used to perform a basic economic analysis of the process by using these two organics selected as model soil contaminants.

An additional aim of this study was to develop scale-up methodology from laboratory SFE devices to industrially useful equipment. Laboratory scale data, such as mass transfer coefficients, have implications for the sizing and control of process units including reactors and separation columns since high mass transfer rates allow smaller reactors. Furthermore, this study included the collection and analysis of the experimental data to support the application of the supercritical fluid extraction technology and to provide the conceptual design and operational processes required for the construction of a pilot plant unit.

The experimental data were presented as an outlet concentration profile of solute (naphthalene or 1,2,4 trimethyl benzene) desorption at different flow rates. This qualitative analysis of the desorption experiments suggested that a promising model should include external and intraparticle mass transfer and be based upon equilibrium at a desorption site. Thus, a simulation has been performed using an equilibrium desorption model [1] and fitted using MATHEMATICA© software (version 2.2.2). Finally, a preliminary economic analysis using these results showed that the proposed process (SFE) is feasible for soils contaminated with two different pure (naphthalene or 1,2,4 trimethyl benzene) hazardous organics as a model system.

INTRODUCTION

There are currently many treatment technologies which are being used or proposed for remediation of contami-
nated environmental matrices. A destructive technology such as conventional thermal incineration has the ability to treat contaminated soil and sediments. A significant amount of applications data exists on thermal incineration. This technology can destroy polychlorinated biphenyls (PCBs) and leave no toxic solvent [2]. However, incineration produces an ash with a high concentration of heavy metals. Furthermore, incineration generally suffers from poor community acceptance. Moreover, to obtain a permit to destroy wastes containing hazardous agents such as PCBs, the process must be able to demonstrate conformance with the requirement of 99.99% destruction and removal efficiency [2]. Typical costs are in the range of $1713 to $1826 per cubic meter of material treated or processed [3].

Thermal incineration is implemented by thermal stripping or volatilizing the organic contaminant compounds from the soil matrix by the application of extreme high temperature ($> 600°C$) and long residence times. During the process a device, which usually utilizes a 23 million btu/hr rotary kiln as the primary combustion chamber, heats the soil and most of the hydrocarbons are driven from the soil, either vaporized, collected, or transformed to carbon dioxide, but not much is left in the soil [4]. After this classical process is completed, the soil is no longer alive or productive. The organic matter component of the soil has been oxidized to CO_2, the established microflora destroyed, and the mineral component of the soil has lost the water and hydroxyl groups that constitute its structure. It is impossible to have a soil that will support plant growth after an incineration remediation treatment [4].

Biological treatment technology or bioremediation is the process of using microorganisms to detoxify or decompose degradable organics. Biodegradation of PCBs as a remedial technology is in the development stages [2]. Several studies have discovered microbes, such as species of Achromobacter, Alcaligenes, and Pseudomonas, which exhibit an ability to degrade specific PCB congeners to varying degrees. Best results can be obtained in biological reactors which can operate with the required aeration, mixing, residence time, temperature control and nutrient delivery to optimize the biokinetics [2].

Bioremediation offers two advantages over thermal incineration: on site destruction of the contaminants and lower total remedial costs. Biological technologies are living systems in which survival of the necessary microbes is vital for this technology to be feasible. Therefore, it is necessary to conduct treatability testing on actual waste samples to evaluate the ability of the microorganisms to de-

grade the specific PCB congeners present or even survive [2]. The lack of information on field applications of biologicalprocesses to remediate PCB contaminated wastes makes it difficult to specify levels of detoxification possible in non-laboratory conditions. Likewise, it is not possible to quantify chemical or matrix interferences which may be encountered, or the costs to be expected on a per unit basis [2]. However, bioremediation has generated interest as a process for treating contaminated soils or sludges in both Europe and the United States. Biological treatment costs range from approximately $300 to $350 per cubic meter, which is comparable to other on-site remediation technologies [3].

On the other hand, supercritical fluid extraction operating parameters are less destructive than thermal incineration conditions and more readily delineated than bioremediation techniques. The unique characteristic of the SFE technology is that a supercritical fluid is more like a gaseous phase, and can diffuse through the interstitial spaces of solid materials much more readily than liquids. This allows the supercritical fluid to make intimate contact with any substance that is sorbed to the solid material, facilitating removal of the contaminant. The attractive physicochemical properties of supercritical fluids qualify them as a viable alternative to conventional solvents used in extraction processes.

Advantages of using SFE as a clean up process include the lack of solvent toxicity, the ability to recover the contaminants and solvent, possible economic benefits and the ability to remediate sites that can not be treated with conventional technologies. Carbon dioxide extraction would not require as much energy as soil incineration and it would leave the structure and nutrients in the soil relatively unchanged.

Recently, there have been studies of the application of this technology at the bench scale for extraction of organic compounds, specifically as treated to removing pesticides from soils [5]. Similarly, Caprie et al. [6] used supercritical methanol to extract bound pesticide residues from soil and plant residues. Schantz and Chesler [7] used supercritical CO_2 to extract polychlorinated biphenyls (PCB) from sediment and polycyclic aromatic hydrocarbons (PAH) from urban particulate matter. Supercritical CO_2 also has been used to remove hexachlorocyclohexane, PCBs, and PAHs from Tenax packing [8]. A significant amount of work concentrated on activated carbon regeneration, such as desorption of phenol [9], pesticides [10], acetic acid [11], and arochlor [11], and ethyl acetate [(12].

The results of these previous studies have demonstrated at the bench scale that it is possible to extract contaminants with molecular weight as high as 400 at mild operating conditions and to carry out the process selectively if desired [13]. A preliminary economic evaluation for a full-scale system indicates total treatment costs for remediating soils by supercritical extraction range approximately from $60 to $200 per cubic meter of soil [14].

SCALE-UP STRATEGY

The U.S. Environmental Protection Agency (EPA) has searched approximately 36,000 abandoned wastes sites in the United States. Over 1,200, those considered the most hazardous, have been located on the National Priorities List (NPL) for cleanup under Superfund [15]. Actual clean-up technologies are not sufficient to deal with the enormous site remediation problem. Some proven remedies are very costly and long period of time consuming, and many of the technologies used to date do not address the more complex problems faced at some sites. Consequently, there is a need for more effective, less costly remediation technologies [15].

The demand for technologies to clean-up contaminated soils without incorporating additional contaminant is increasing. One approach to solving this remediation problem is the use of supercritical fluids to extract contaminants from the soil. There are several studies on the extraction of organics compounds from soil using supercritical fluids like carbon dioxide, alone or with cosolvents, on a laboratory scale.

Cassat and Perrut [16] have proposed a transportable extraction equipment which uses a semi-batch operation for on-site soil cleaning. They have designed a unit capable of extracting 800 kg PCB's per day from scraped soil [17]. Rice [18] has operated a slightly different type of apparatus for extracting soil with supercritical carbon dioxide. Rice [18] has reported 99.7% removal of xylene from soil using the modified apparatus [17].

Supercritical extraction has been demonstrated in the literature at the bench scale for extraction of organics from soil, there are few systems which have been commercially implemented. One such system has been developed by Critical Fluid Systems Corporation for remediation of soils [19]. The process uses supercritical propane on contaminated solids and SC-CO_2 to treat wastewater. In this process, the soil is transported to a high pressure heated reactor and the supercritical solvent is flowed over the soil until the desired level of decontamination is achieved. The solute is then separated by pressure reduction and the fluid is compressed back to the operating conditions. However, the system suffers from two major effects, the high energy consumption due to the recompression of the fluid, and the condensation of the extract that can cause plugging the pipes. The energy required for the recompression of the fluid recycle to the operating condition is high due to the fact of the high pressure drop during the precipitation of the solute. The precipitation of the extract in the lines leads to clogging of the piping and valves, and established the need to install additional equipment to avoid possible shutdowns, which might occur due to the plugging [14].

Recently, Madras et al. [14] have proposed an optional scheme for removal of organic compounds from soils using SC-CO_2. This scheme includes the use of an activated carbon bed to strip the extracted contaminants from the CO_2 stream enables to operate the system with a back-pressure regulator instead of a restrictor (expansion valve) heated above the melting point of the organics. The costs are less for this proposed process due to the fact that it is not necessarily a costly re-compression stage. The deposited contaminants on the activated carbon bed can be destroyed by the classical incineration [14]. An industrial scale application of a similar process, based on the same principles, is carried out in Germany [20].

Continuous solids extraction with supercritical fluids is complicated by feeding the solid material from ambient pressure to the high pressure extractor [21]. The continuous mode is interesting because it would reduce the volume of high pressure equipment per the amount of treated

soil [17]. This would be a great economical advantage in a high pressure process. One approach is mixing the soil with water and then the mixture is slurried so that they can be pumped to the extractor [17]. This alternative was presented by Agkerman and Yao [21]. Finally, Torossian et al. [22] have patented a procedure and an apparatus for continuously extracting soil by high pressure fluids [17].

Based on our preliminary work and the studies of others [23, 24, 25], conditions in laboratory scale SFE result in low Reynolds number flow $(1 < N_{Re} < 50)$. Under these conditions buoyancy forces are significant and the appropriate scaling factors include the effect of Grashof number (N_{Gr}) in correlating the data. A significant scale up consideration is the higher flow rates, and higher N_{Re}, presumably required in commercial processing such as used in the decaffination of coffee beans $(320 < N_{Re} < 3500)$ [26]. Finally, the capital and operating costs of our proposed, optimum commercial supercritical fluid extraction design will provide a reliable economic comparison with other remediation technologies.

EXPERIMENTAL WORK

Semi-Continuous Apparatus

A process schematic of the bench-scale supercritical fluid extraction system is shown in Figure 1. The operating principle of soil extraction with supercritical CO_2 is based on a semi-continuous mode. In this mode of extraction a batch of soil containing a known quantity of contaminant is packed in the extraction cell. The cell is pressurized and a continuous flow of supercritical CO_2 is then pumped through the porous solid. The supercritical CO_2 flows through the extraction cell removing the organic contaminant from the soil. The experiment continues until all of the contaminant is removed or the operating time becomes greater than about 600 minutes. After extraction the solid is depressurized and discharged from the cell at atmospheric

pressure. The desorption profiles of the organic are calculated from these set of data collected. Details of the experimental set-up and procedures are provided elsewhere [27].

Soil Considerations

Soil is a complex mixture which can be divided into two major components: inorganic phase and organic phase [28, 29]. The inorganic phase in soils further is divided as sand, silt and clay fractions. The organic phase is subdivided into humic and non-humic fractions. The humic materials are classified as fulvic acids, humic acids and humins. The non-humic parts consist of the organic materials which include amino acids, fats, resins, waxes, and are the biodegradable fraction of the organic phase. A simple schematic diagram of soil composition is shown in Figure 2.

Due to the fact that soil is a complex matrix, the success of an efficiency extraction operation depends on the soil type. Soils which contain more organic components are usually difficult to clean by extraction because the organic contaminants tend to bind strongly in the organic matter in the soil. On the other hand, clays have high contents of Al^{3+} and Fe^{3+}, which can absorb organic acids and bases and highly polar non-ionics [30].

Additional soil characteristics which can have an effect on the soil extraction result are the moisture, particle size, surface area and porosity. The moisture of the soil will influence the adsorption of the contaminant in the soil, the equilibrium distribution of the contaminant between the solid and fluid phases, and the extraction rate [17]. Soil particle size affects the adsorption capacity. If the soil particles are small the surface area of the soil will be large and the adsorption capacity will also be large. Cai [31] found that supercritical extraction rate was less efficient from clays because of the small particle size and high adsorption capacity. Burk et al. [32] found no significant effect of the
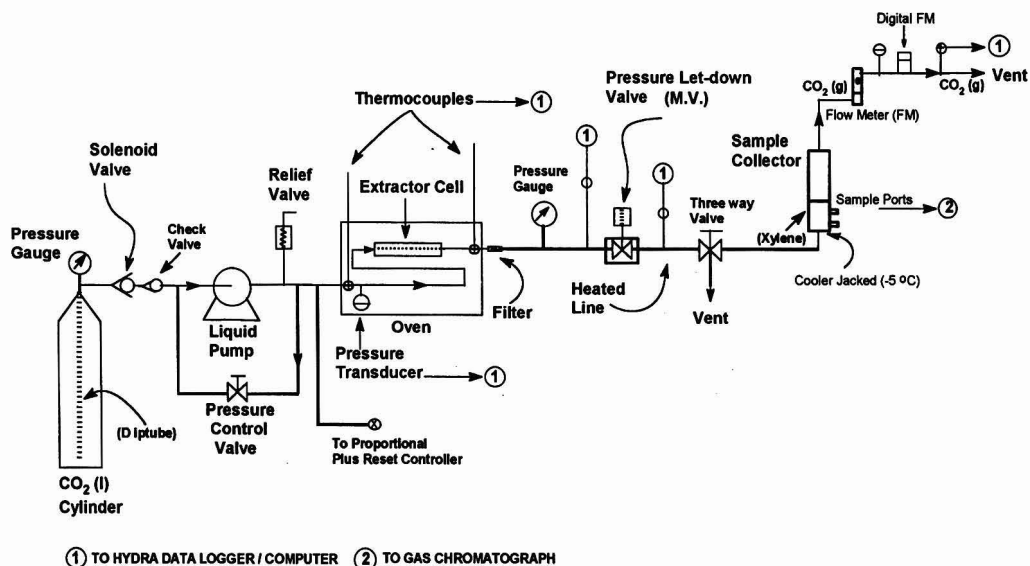

FIGURE 1 Schematic of semi-continuous supercritical fluid extraction experimental setup.
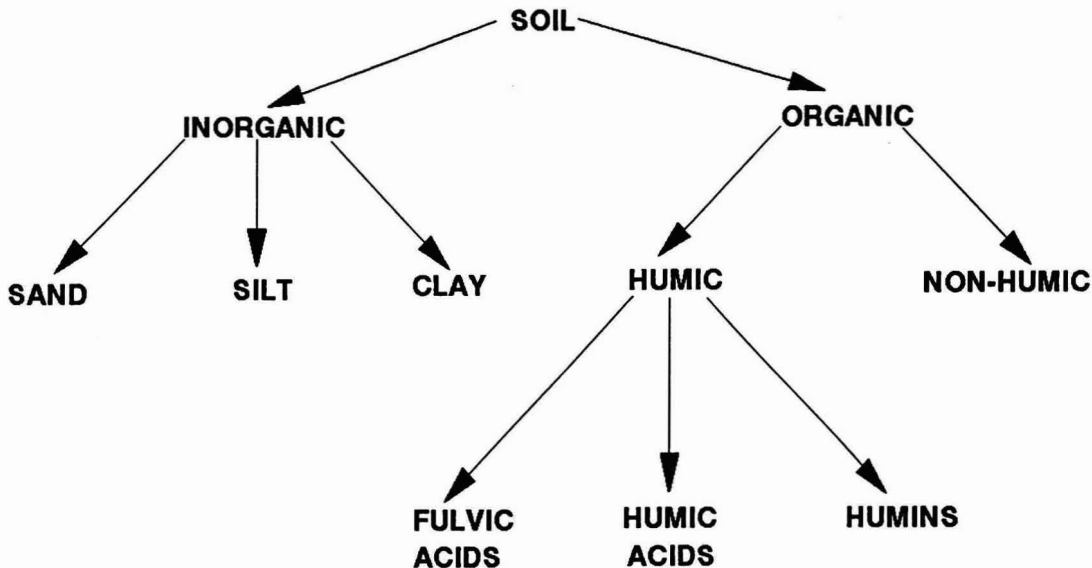
FIGURE 2 A schematic diagram of the composition of soil.

particle size on the extent or rate of removal of fluoranthene from sand and Cai reported only a small increase of extraction recovery with increasing sand particle size.

Finally, the complex and heterogeneous structure of soil makes modeling studies for transfer of SFE technology from laboratory scale to real waste sites extremely difficult [33].

Materials

The liquid carbon dioxide was bone dry grade (99.0%) and it was purchased from Air Products, Inc. The solid naphthalene, supplied by Kenova Chemical Company, was reagent grade of 99.9% purity. The stated purity of naphthalene was verified by gas-chromatograph analysis and subsequently used without further purification. The liquid 1,2,4 trimethyl benzene (TMB), supplied by Janssen Chimica Company, was 98% pure and it was used as received. All other solvents (such as acetone and xylene) were obtained from Fisher Scientific and were used without further purification.

Soil Screening and Preparing Soil Samples

Uncontaminated soil (gravel, sand, and fines which included silts and clays) was obtained from a site at Argonne National Laboratory in Argonne, IL. The moisture content in soil as received was approximately 17.2% and the total organic content was 3.0% (ASTM D-2974). U.S. standard screens were used to measure the size of particles. The soil was sieved for ≈ 60 minutes. The Tyler standard sieve series was comprised of screens whose mesh size was 0.0937 in, 0.0661 in, 0.0555 in, 0.0469 in, 0.0394 in, and 0.0331 in. The experimental procedure was designed to reduce soil "clumps" prior to screening and to remove materials such as rocks, rubble and gravel. The soil screening equipment is a Testing Sieve Shaker (RO-TAP)/The W. S. Tyler Company (Model No. 5451). The organic content in solid after sieved was 3.6%.

Wet soil was first dried at 383 K in shallow glass containers in a radiant heat oven (Lab-Line Instruments, Inc.) overnight. After the soil was dried, it was prepared by grinding the soil with a ceramic mortar and then sieved to 12–14 mesh fraction (the average particle size is 0.0512 in), and finally stored in a sealed glass container. Approximately 28 g of contaminated soil was fed into the reactor for each experiment. In order to achieve uniform CO_2 flow distribution and to avoid possible end effects, glass beads of 0.15 cm diameter were packed in the sections above and below the dry soil packing in the tubular reactor. Soil composition and the specifications of the packed bed were presented in Table 1 by Montero *et al.* [34].

Soil samples were artificially contaminated or spiked by making a slurry of the soil with an acetone solution of the solute (naphthalene or 1,2,4 trimethyl benzene) in glass pan, and allowing the acetone to evaporate in the air. Later on, the solids were transferred to glass storage containers. The initial concentration levels of naphthalene and 1,2,4 trimethyl benzene were approximately 10,000 and 50,000 ± 500 mg/L by weight and then it was verified by conventional solvent extraction before treatment (supercritical extraction). The total amount of solute, which was collected after the extraction, was compared with the initial amount measured in each sample resulting in material balance closure to 99.8 ± 0.2% [34].

RESULTS AND DISCUSSION

In this study experimental data for a bench-scale supercritical fluid extractions of soils adsorbed with naphthalene and 1,2,4 trimethyl benzene have been modeled with the equilibrium desorption/mass transfer equations [1] and the process implications for scale-up feasibility has been presented. Soil samples contaminated with these two model organics were extracted over a matrix of supercritical density and CO_2 flow rate. Various supercritical CO_2 condi-
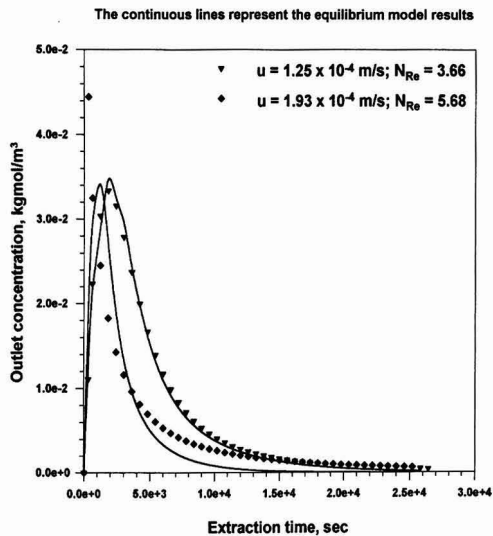
FIGURE 3 Comparison of simulated results (equilibrium model) with experimental data for naphthalene at P = 103 bar and T = 318 K.
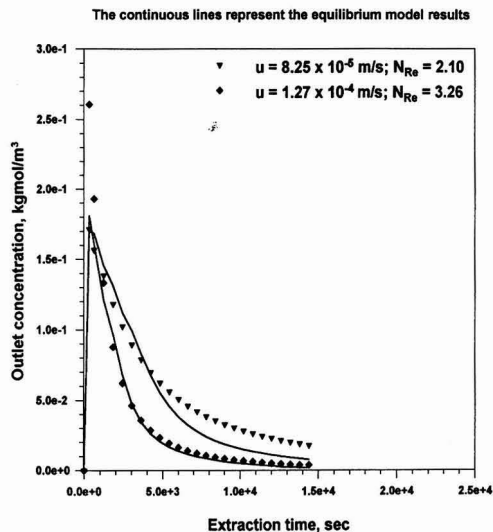
FIGURE 4 Comparison of simulated results (equilibrium model) with experimental data for 1,2,4 TMB at P = 121 bar and T = 308 K.

tions were used in an effort to optimize the extraction parameters.

Desorption from Soil

The concentration of the contaminants was monitored from start-up to a final extraction time (t_e) which is based on the per cent removal for each run. The desorption experiments were carried out with an initial loading of solute of concentration Ca_o. The desorption of organics from soil particles follows three consecutive mass transport steps. First, intraparticle diffusion from the interior to the outer surface of the particle. Second, mass transfer of the organic compounds from the outer surface of the particle to the gas phase. Finally, bulk transport of the organic compounds in the supercritical phase.

Figures 3 and 4 show the experimental outlet concentration profiles of naphthalene and 1,2,4 trimethyl benzene in the effluent at two CO_2 flow rates. The points in Figure 3 (at P = 103 bar and T = 318 K) and Figure 4 (at P = 121 bar and T = 308 K) for the solute extracted from soil represent experimental data and indicate a significant effect of flow rate [34]. This qualitative analysis of the experimental data suggests that a promising simulation model, which can be used to approach the scale-up, should include external and intraparticle mass transfer and be based upon equilibrium at a desorption site. Solute on the solid surface can exist in two states, adsorbed state and the deposited state. The amount of the solute that is deposited as a separate phase on the solid surface is extracted by simple dissolution in the supercritical phase. On the other hand, the extraction of the amount of solute that is adsorbed on the solid phase is controlled by the adsorption-desorption equilibrium. The available experimental information suggests a two-parameter $(k_o$ and K) equilibrium desorption model can be used to analyze the experimental data.

In this work the outlet concentration profiles from dry soil were simulated using an equilibrium desorption/mass

transfer model and the mathematical analytical equations for the outlet concentration in the CO_2 stream with an initial concentration Ca_o in the soil are similar to the ones developed by Recasens for regeneration of activated carbon [1, 35].

The adsorption equilibrium constant, K, and the overall mass transfer coefficient, k_o, were evaluated by fitting the analytical equations with the experimental data. Optimal values for K and values for K and k_o were obtained with the best fit between the experimental data points and the values predicted from the model. The approach to determine parameters from the experimental data was to approximate the external mass transfer coefficient (k_e) and intraparticle diffusivity (D_e) from correlations. With these values as initial estimates, the experimental data were fitted to the concentration profiles [34].

The continuous lines simulated and displayed, using MATHEMATICA© software with graphics capability, are shown in Figures 3 and 4. With the optimal values calculated, K and k_o, the simulated results agreed well with the experimental concentration profiles for the effect of superficial velocities in the range of u = 8.25×10^{-5} m/s (N_{Re} = 2.10) and u = 1.93×10^{-4} m/s (N_{Re} = 5.68) as shown in Figure 3 for naphthalene and Figure 4 for 1,2,4 trimethyl benzene [34]. The results showed that in the range of higher flow rates solubility limits extractions, and lower flow rates are controlled by diffusion limited extractions [34, 36].

Figure 5 shows a comparison between supercritical fluid desorption from granular activated carbon [37] and soil [34] at very similar experimental conditions. Granular activated carbon (GAC) has been used as a matrix model for several studies using supercritical fluids [1, 12, 38]. Tomasko et al. [37] have presented an economic evaluation of the pilot plant results which applied to the design of a fixed-site GAC regeneration unit consisting of a three-element desorber with two-stage flask separation. The economic analysis shows a processing cost of $154 per cubic
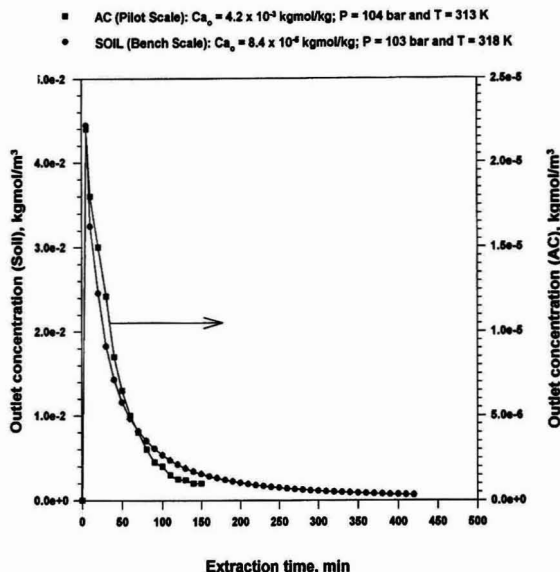
- AC (Pilot Scale): $Ca_o = 4.2 \times 10^{-3}$ kgmol/kg; P = 104 bar and T = 313 K
- SOIL (Bench Scale): $Ca_o = 8.4 \times 10^{-6}$ kgmol/kg; P = 103 bar and T = 318 K

FIGURE 5 Comparison between supercritical fluid desorption from granular activated carbon and dry soil.

meter of GAC which compares favorably with thermal regeneration and incineration. Figure 5 shows that the time required to decontaminate GAC in a pilot scale apparatus (fraction removed of 2-chlorophenol ≈ 0.95) is almost 100 minutes less compared with contaminated soil in a bench-scale (fraction removed of naphthalene ≈ 0.99). The trends of the two curves are quite good despite differences in temperature, superficial velocity, initial loading concentration (Ca_o) and solid matrix (activated carbon which has a very long tail compares with soil).

The removal efficiency is determined by two different effects, solvation and adsorption. The solvation is predicted by thermodynamic equilibrium and can be calculated using equation of state models for solid-supercritical fluid phase equilibria. On the other hand, the adsorption properties are defined by the characteristics of the activated carbon or soil and the contaminant type [37].

SCALE-UP ANALYSIS

As a preliminary analysis, the scale-up for SFE of soil contaminated with naphthalene and 1,2,4 trimethyl benzene has been simulated by using the equilibrium desorption model. This was used to evaluate the effect of superficial velocity over practical ranges. The determination of the optimal superficial velocity was approached by increasing

the flow rate until further increments no longer result in decreased extraction time. The results for the simulation at $u = 4 \times 10^{-2}$ m/s are shown in Figure 6. The previous values for the adsorption equilibrium constant (K) and mass transfer coefficient k_o) at the highest superficial velocities ($u = 1.93 \times 10^{-4}$ m/s for naphthalene and $u = 1.27 \times 10^{-4}$ m/s for 1,2,4 TMB) were used as initial value for the calculation of the outlet concentration profile for the scaled-up extractor. Representative fitted values of K and k_o for the model organics are presented in Table 1.

Flow rate (superficial velocity) is an important variable in the design of scale-up supercritical fluid extraction process. For each pilot-scale or commercial-scale SFE process and for each extraction application there is an optimal flow rate [36]. This optimal flow rate may vary with extraction time. Excessive flow will lead to insufficient loading of the solvent, and in severe cases "compacting of the bed," thereby producing a large pressure drop, which most likely will result in channeling through the bed and inefficient extraction. On the other hand, small flow entails very long extractor residence times which leads to an uneconomical extraction process [36]. In most cases the flow rate of a supercritical fluid extraction system will be about 10–30 kilograms per hour per kilogram of feed material in the extraction vessel [36].

The proposed scheme for extraction of soil and details of the process, which operates in the optimum mode, are given elsewhere [13, 14]. The simulation data (Figure 6) for the model organics indicate the mass transfer kinetics are limiting. Hence the outlet concentrations profile are not approaching the equilibrium concentration (C*) in supercritical CO_2 limits at any time, most evidently during the last half of the desorption extraction time.

FEASIBILITY OF A PILOT-SCALE SFE UNIT

To illustrate the commercial potential and the economic feasibility of the supercritical extraction process, capital and operational costs have been evaluated for a system that can be transported and which is capable of treating soil contaminated with the model organics investigated in this work. The chief design parameters needed for a SFE process are properties of the raw material (soil in our case), the required production rate, the concentration of extractable contaminants in the feed, the kind of raw material for extraction, the specific volume of the feed, and the mode of operation [39]. Other important parameters which influence the process and the design of a plant are given in Table 2.

In the range at the supercritical region the influence of pressure, temperature, and density of the solvent on the distribution equilibrium are more important than in conventional extraction. In the extraction step it is desirable to

TABLE 1. Equilibrium Constant, Kρ and Overall Mass Transfer Coefficient, k_0 for Naphthalene and 1,2,4 Trimethyl Benzene

PURE NAPHTHALENE				
u = 0.04 m/s	N_{Re} = 1,200	$k_e = 1.6 \times 10^{-3}$ m/s	Kρ = 1.3	$k_o = 1.7 \times 10^{-7}$ m/s

PURE 1,2,4 TRIMETHYL BENZENE				
u = 0.04 m/s	N_{Re} = 1,000	$k_e = 1.2 \times 10^{-3}$ m/s	Kρ = 2.0	$k_o = 5.8 \times 10^{-7}$ m/s

- Naphthalene: $Ca_o = 8.4 \times 10^{-4}$ kgmol/kg; $P = 103$ bar and $T = 318$ K
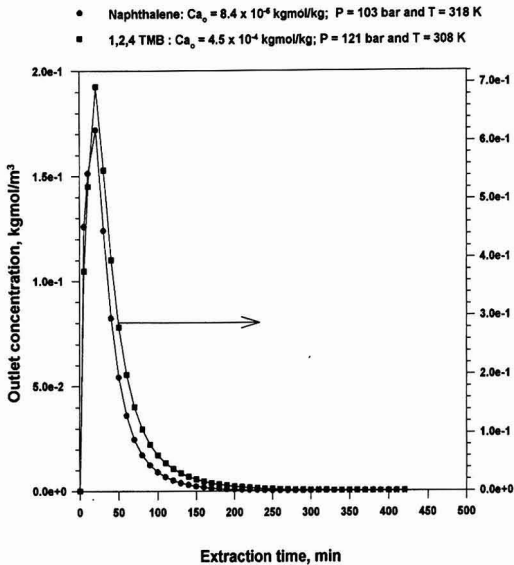- 1,2,4 TMB : $Ca_o = 4.5 \times 10^{-4}$ kgmol/kg; $P = 121$ bar and $T = 308$ K

FIGURE 6 Calculated outlet concentration profile of naphthalene and 1,2,4 trimethyl benzene for scaled-up extractor.

reach a high solubility and therefore a low solvent consumption. In the separation step a very low concentration of the extract in the solvent is required to guarantee a good regeneration of the solvent [39].

Costs are generated based on data collected from a bench-scale operating treatment system [14, 40]. A cost summary, with a breakdown by mainly category, for the process is presented in Tables 3 and 4. The system cost and capacity are scale-up to a pilot plant system. The equipment costs have been taken from Novak et al. [41], based on supercritical fluids proprietary process and plant design data. A summary of the direct capital costs is given in Table 3. Indirect costs are estimated as 38% of direct costs, then fees and contingencies are 25% of direct plus indirect costs. The cost of excavation and transportation used in Table 4 is taken from an EPA report [42]. The labor costs include direct cost, supervision and personnel. Materials, supplies, and utilities include direct costs plus a markup. The depreciation, taxes and insurance, plant overhead and administrative costs included in the operating costs are directly related to the capital cost of the pilot-plant (as shown in Table 4).

The annual capacity of the process changes for each organic because the cycle times for each organic varies since the time required for the SC-CO_2 to remove the organic from soil is dependent on the specie being extracted [14].

TABLE 2. Design Parameters for a Pilot-Scale Supercritical Extraction Process

Treated Medium	Contaminated Soil
Textural Analysis of Soil	Graval, sand, and fines (silts + clays)
Model Organics	Naphthalene and 1,2,4 TMB
Contamination Levels	10,000 mg/L and 50,000 mgL
Extractors (1/d) = 10; Solid Volume	3.35 m³
Bed Porosity	0.4
Bed Density	1120 kg/m³
Optimum Extraction Temperature	308 K
Extraction Pressure Range	(120–330) bars
Extraction Fluid	SC-CO_2
Circulation Rate	20 m³/hr
Continuous Operation	24 hrs/day, 300 days/yr

TABLE 3. Capital Costs for the Transported Pilot-Plant

Equipment Description[1]	Design Pressure	Size[2]	Estimated Cost[3,4] ($)
Two Extraction Vessels[3]	330 bar	3.90 m³	691,400
Adsorbed Bed[4]	330 bar	3.90 m³	384,000
High Pressure Liquid Pump[3]	450 bar		44,000
Solvent Recycle[4]	330 bar	20 m³/hr	44,000
Valves and Accessories	330 bar		15,000
Instrumentation	450 bar		100,000
Recycle Compressor[3]	450 bar		49,000
Total Equipment Costs (Direct Costs)			1,327,400
Indirect Costs[3] (38% × Direct Costs)			504,412
Fees and Contingency[3] (25% × (Direct + Indirect))			457,953
Total Capital Costs (T.C.C.)			2,289,765

[1]The costs of the equipment are increased using the six-tenths factor [43].
[2]The sizes have been quadrupled [41].
[3]Tomasko et al. [37].
[4]Madras et al. [14].

TABLE 4. Summary of Operating Costs $/m³ Soil

Item Description	Remarks	Naphthalene	1,2,4 TMB
Annual Capacity	m³ of soil decont./yr	7236	5790
Cap. of Activated Carbon[5]	g adsorbed/g carbon	0.25	0.23

Basis: 1 m³ contaminated soil			
Item Description	Remarks	Cost ($/m³)	Cost ($/m³)
Transfer of soil into vessel	Excavat. & Transport.	40	40
Make-up CO_2	100 kg/Cyc. ($0.1/kg)	2.71	2.71
Operating Labor (L)	1 per shift, $15/hr	15	19
Direct Supervision (S)	$15/hr	15	19
Utilities (electricity, heating)	$5.0/hr	10.59	10.59
Maintenance (M)	4% of T.C.C.	12.66	15.82
Operating Supplies	15% of Maint.	1.90	2.37
Adsorbent Incineration	$1.7 kg	7.62	8.28
Adsorbent Replacement	$2.0 kg	8.96	9.74

Fixed Charges			
Depreciation	15 yrs, $2,289,765	21.09	26.36
Taxes and Insurance[5]	1.5% of T.C.C.	4.75	5.93
Plant Overhead[6]	60% of (L + S + M)	25.60	32.30
Administrative Costs[6]	15% of (L + S + M)	6.40	8.19
Total Operating Costs (T.O.P.)		172.29	200.24

[5]Madras *et al.* [14].
(6)Tomaski *et al* [14].

The extraction time required to clean up the soil (100% decontamination) loaded with 10,000 mg/L of pure naphthalene and 50,000 mg/L of pure 1,2,4 trimethyl benzene was found, using the equilibrium desorption model (Figure 6), to be 200 and 250 minutes respectively.

The major costs of the operating costs, for the model organics evaluated, stems from the cost involved in the transfer of the soil to the extraction vessel. The cost calculations and analyses are based on naphthalene and 1,2,4 trimethyl benzene and a deeper details of cost estimate assumptions are given elsewhere [14, 37, 41].

Table 5 shows a comparison of operation costs of the processed process with other alternative technologies for soil remediation [3]. Considering that the operational costs for these technologies are based only on treatment and exclude any operational costs on capital, the proposed process seems technically attractive. This process compares favorably both economically and ecologically with the alternatives.

Recently Chen *et al.* [44] have presented an economic analysis of the supercritical fluid extraction as a remediation technology. They estimated the costs for a plant (1 m³ vessels) which would reduce the concentration of PCBs (such as Arochlor 1248) in soil from an initial concentration of 1,000 mg/L to below 5 mg/L residual PCB with a contact time between 30 to 90 minutes depending on soil type, level of contamination and conditions of contacting. The total cost would be $200 per cubic meter sand in a plant that would treat 24,000 m³ contaminated sand per year [17].

CONCLUSIONS

The process operated on a semi-continuous mode and the results indicated that the recovery of extractable material depended on the solvent flow rate. The specific system studied, the extraction of contaminants from soil, has several interesting features, some of which are of general applicability and some quite specific to remediation of soil.

Not unexpected the highest extraction rate and the final recovery level of naphthalene and 1,2,4 trimethyl benzene were at P = 121 bar and T = 308 K, due to the increased value of the supercritical fluid density (ρ co$_2$) at this experimental condition.

The nature (total organic carbon content) and character of the soil and the interaction between soil and contaminant have to be taken into consideration.

The limitations of the equilibrium model were apparent when simulation were attempted for the lower superficial velocity ($N_{Re} \leq 1$). Therefore, the model unsuccessfully fit the breakthrough front of the experimental concentrations

TABLE 5. Comparison of Operating Costs for Remediation of Soil

Process Name	Cost ($/m³)
Supercritical Water Oxidation	250–733
KPEG	211–378
O.H.M. Methanol Extraction	400–514
Acurex Solvent Wash	196–569
Vitrification	255–548
Bio-Clean	191–370
Soilex Solvent Extraction	856–913
Chemical Waste Landfill	260–490
Incineration	1713–1826
Supercritical Fluid Extraction	170–200

profiles, however it was successfully in fitting the elution tail [34].

A economic evaluation for a pilot-scale system based on the experimental data from the bench-scale system indicates total remediation costs of approximately $170 to $200 per cubic meter.

The cost analysis of the proposed process showed that the highest cost was projected for the excavation and transportation of the soil from the site to the high pressure vessel.

Supercritical fluid extraction (SFE) is a viable alternative for remediation and restoration of contaminated soils.

ACKNOWLEDGMENT

NOTATION

AC = activated carbon
C = concentrations of adsorbate in bulk fluid, kg-mol/m^3
C_a = adsorbed solute concentration, kgmol/kg
Ca_o = initial adsorbed solute concentration, kgmol/kg of soil
$C(L, t)$ = outlet concentration in the bed effluent, kgmol/m^3
C^* = equilibrium concentration in SC-CO_2, kgmol/m^3
D_{ab} = binary diffusion coefficient (solvent-solute), m^2/s
D_e = effective diffusivity in the porous particles, m^2/s
d = extractor diameter, m
d_s = diameter of sample, m
K = adsorption equilibrium constant, m^3/kg
k_e = external mass transfer coefficient [45]s, m/s
k_o = overall mass transfer coefficient, m/s
L = bed length, m
N_{Re} = modified Reynolds number ($N_{Re} = ud_s\rho/(1 - \alpha)\mu$), dimensionless
P = pressure, bar
P_c = critical pressure, bar
r_o = soil particle radius, m
T = temperature, K
T_c = critical temperature, K
t = time, s
t_e = extraction time, minutes or seconds
u = superficial velocity of fluid at T and P of bed, m/s

Greek Letters

α = bed void fraction
β = porosity of particles
μ = viscosity of the fluid, kg/m s
ρ = density of particles, kg/m^3

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Wastewater Treatment Enhanced by Electrochemistry

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Since the late 60's DIAMO, in the Czech Republic, has mined uranium via in-situ acid leaching. Sulfuric acid is injected into underground uranium deposits, dissolving the ore. The solution is then pumped to the surface where the uranium is separated from the acid. The spent acid is injected into underground caverns. Over the years, this subterranean acid waste lake has grown and now threatens the local drinking water supply.

Researchers at ELTECH Systems Corporation have developed an electrochemical process for Ionics Incorporated and their Resources Conservation Division as part of a system that will clean up 2.7 million gallons (10.2 × 10³ M³/day) of sulfuric acid waste a day, recover 936 tons per day (850 mT/day) of ammonium aluminum sulfate crystals and reclaim 2 million gallons a day (7.6 × 10³ m³/day) of water. The electrochemical portion of the process will convert Fe^{+3} in a solution of raw ammonium aluminum sulfate crystal to Fe^{+2}, so pure ammonium alum can be crystallized.

This paper discusses the engineering fundamentals used to develop the electrochemical iron reduction system for the DIAMO application. Initial work included cyclic voltammetry to characterize cathode candidates, identify significant reactions, and show feasibility. This was followed by tests at the bench scale, the intermediate scale, and finally at the pilot scale using commercial size electrodes. The cell design evolved concurrently with the bench and pilot work, culminating in a commercial, skid-mounted unit for the full size plant.

DIAMO SITUATION

Large underground reservoirs of contaminated water created by acid mining, slowly increased in volume to the point where the hydraulic load threatened to cause overflow of acid waste into the clean water aquifers. Spurred by the impending danger, Diamo committed to remediation of the site. The technology chosen was desalination to remove the acid salt, coupled with crystallization to remove and recover the acidic ammonium alum that had

accumulated in the reservoirs. The job was awarded to Resources Conservation Company International (RCCI), a subsidiary of Ionics Incorporated.

RCCI is presently constructing a system to recover 1600 GPM (6.1 M³/min) of high quality water distillate from the acid leachate which can be safely discharged to the environment. Ammonium aluminum sulfate is recovered by concentrating the feed seven times utilizing specialized evaporators followed by flash crystallization. However, in order to provide the highly purified alum required, it is necessary to reduce the level of Fe, Ca, Na, Mg, K, and SiO_2 in the raw crystal. For the most part this is done by the incorporation of a recrystallization/filtration setup. Ferric ions, however, are easily incorporated into the ammonium aluminum sulfate crystal structure making it impossible to achieve the desired low iron level without additional treatment. Since ferrous iron is not similarly coprecipitated, reduction of the Fe^{+3} to Fe^{+2} before crystallization produces the required product purity. While all the other unit operations in the overall system were common industrial practices, the iron reduction unit was not. An approach had to be developed that was technically and economically viable with an acceptable level of risk.

ELECTROLYTIC APPROACH SELECTED

A number of alternatives were considered before the electrochemical reduction system was chosen. The common reducing agents tested proved to be ineffective or uneconomic. For example, aluminum foil strips were found to be a simple process for iron reduction, requiring a short retention time in a tank at a controlled pH. The theoretical consumption of aluminum is 161 g/Kg of Fe^{+3} reduced, but the practical consumption was 320 g/Kg. A major drawback was the difficulty of obtaining a reliable supply of the metal delivered to the plant site. It would have to be imported with pricing subject to variable market conditions.

Alternatively, electrolysis was considered, utilizing electrons for the reduction process. The addition of one elec-
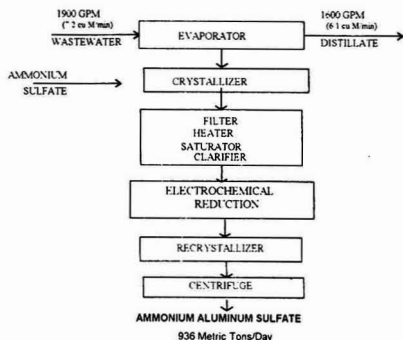
FIGURE 1   Simplified DIAMO block flow diagram.

tron is required to reduce Fe^{+3} to Fe^{+2} the energy required is approximately 2.0 KWH/Kg Fe^{+3} reduced. The electrolytic system requires more equipment, but utilizes readily available electricity on site. Ultimately this approach was chosen because it was the most economical and had no inherent logistic problems.

DIAMO Process Description

A simplified block diagram of the DIAMO evaporator/crystallizer/electrolyzer process is shown in Figure 1.

The main components in the feed to the electrochemical process are shown in Table 1.

In order to meet the requisite alum product purity, the electrolytic process had to reduce the Fe^{+3} from 1285 to 285 ppm by the one electron reduction. Due to this low iron concentration, it was felt that the rate of reduction to Fe^{+2} would be primarily mass transfer limited and that the maximum current density could be estimated by the following equation:

$$I_{limiting} = zFDAC_b/\delta \text{ (Bockris/Reddy, 77)}$$

where: z = number of electrons per equivalent, 1
  F = Faradays constant, 9.65×10^4 amp seconds
  D = Diffusion Coefficient, estimated at $\sim 2 \times 10^{-6}$ cm^2/sec for Fe^{+3}
  A = Electrode Area, basis of 1 sq cm
  C_b = Fe^{+3} concentration, moles/cc
  δ = diffusion layer thickness, estimated at $\sim 1 \times 10^{-3}$ cm

TABLE 1. DIAMO Electrochemical Feed Composition— Major Components

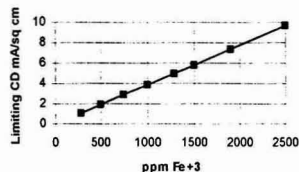| Component	Units	Quantity
SO_4	ppm	166300
Free H_2SO_4	ppm	1830
Al	ppm	20800
NH_4	ppm	14930
Fe^{+2}	ppm	2480
Fe^{+3}	ppm	1285
NO_3	ppm	167
F	ppm	36.0
Temp	°C	70
Flow	GPM	570

FIGURE 2   Estimated limiting current density vs. Fe^{+2} concentration.

Figure 2 is a plot of estimated limiting current density versus Fe^{+3} concentration which provided a "first guess" in determining the desired cathode current density and area.

In order to verify the limiting current density relationship with iron concentration, it was necessary to develop empirical relationships. Selection of an acceptable cathode material was essential to technical and commercial success. The cathode had to meet the following criteria:

1. To avoid corrosion, the cathode must be electrochemically stable at the potential/pH region experienced during operation.
2. Since the ultimate operating current density would be low, the cathode material needed the ability to be made into a structure with very high ratio of actual to projected area. Such a structure would maximize the overall operating current density and minimize the cell area needed for the plant.
3. The chosen cathode structure must be economically attractive and capable of manufacture by standard methods on machines presently available in our manufacturing plant.

Bench Tests

In order to carry out the development of the cathode and define the system operating conditions, a bench test system was set up as shown in Figure 3.

Table 2 provides bench scale system parameters.

The anode compartment was created by gluing a porous diaphragm to a CPVC anode chamber. The diaphragm was ELRAMIX™, a porous composite of PTFE and zirconia. A DSA® coated single layer expanded Ti mesh anode was used. The cathode compartment was defined by the ELRAMIX diaphragm and the walls and bottom of the electrolyzer and the anode frame. It contained a high surface area cathode. Various cathodes were tested and are described later. Fe^{+3} and total iron were determined using a HACH titration method.
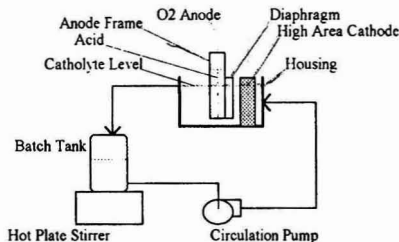

FIGURE 3   Bench test system.

TABLE 2. Bench Scale System Parameters

Cathode Active Area	18 sq inches (116 cm^2)
Catholyte Circulation Rate	1 L/min
Cathode Current Density	37.7 or 21.5 mA/cm^2
Temperature	60°C
Anolyte	0.25 wt% H$_2$SO$_4$
Diaphragm	ELRAMIX^{TM*}
Catholyte Volume	3 L

*ELRAMIX is a trademark of Eltech Systems Corporation.

Selection of a stable cathode material was initiated by a review of the thermodynamic data, available in the Pourbaix Diagrams. Nickel, Silver coated Nickel, graphite, stainless steels, and tin were initial candidates for screening. The actual potential the electrode would operate in the acidic alum feed was not known: just the reversible potential of the iron reduction reaction at the feed pH. Therefore, cyclic voltammetry tests were conducted on nickel, tin, Hastalloy C, Steel Alloy AL6XN, graphite, and DSA coated titanium (Figures 4 through 9).

The cyclic voltammogram for nickel, Figure 4, indicated that the nickel was being oxidized. This was verified in bench cell tests. Upon inspection of nickel cathodes operated for 2–3 hours, severe corrosion was noted and the calculated current efficiency was greater than 100%. A cementation process which caused the Fe^{+3} to be reduced and the nickel to corrode (nickel oxidation) was postulated to explain efficiencies over 100%.

$$Fe^{+3} + Ni^o \rightarrow Fe^{+2} + Ni^{+1}$$
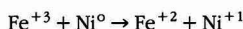
The cyclic voltammogram for a tin cathode, Figure 5, again showed high current densities due to tin oxidation. The steel (AL6XN Fig. 6, and Hastalloy C Fig 7) materials, graphite (Figure 8), and DSA coated titanium (Figure 9) showed no evidence of oxidation or corrosion.

From the cyclic voltammograms, it became clear that there were two important parameters in selection of the cathode: corrosion resistance and the difference between
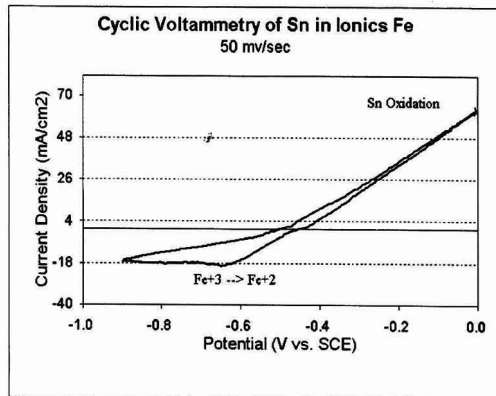

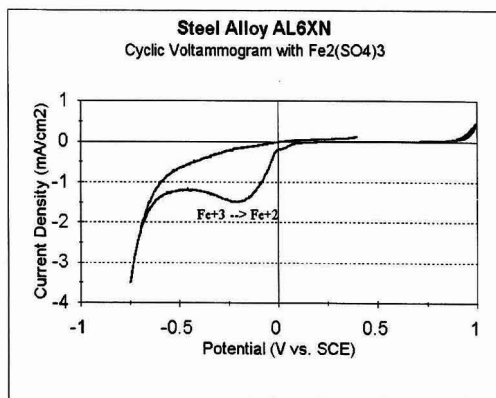**FIGURE 5**   Cyclic voltammetry of Sn in Ionics Fe.

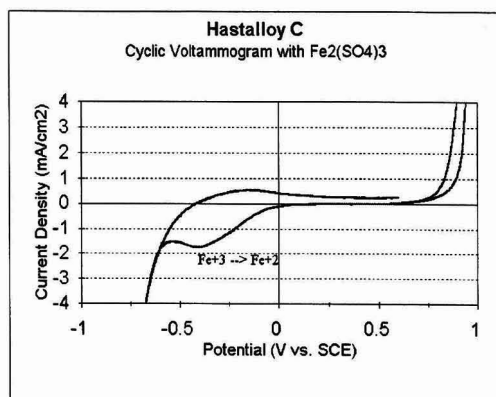**FIGURE 6**   Steel alloy AL6XN. Cyclic voltammogram with Fe$_2$(SO$_4$)$_3$.

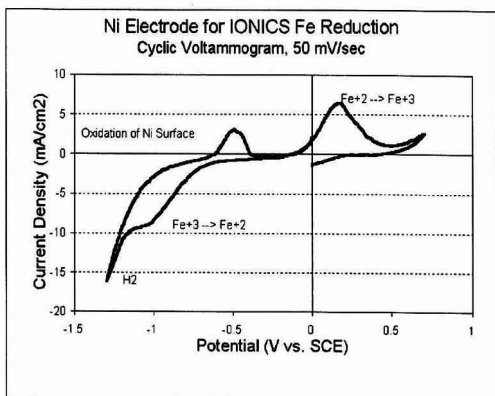**FIGURE 7**   Hastelloy C. Cyclic voltammogram with Fe$_2$(SO$_4$)$_3$.

FIGURE 4   Ni electrode for ionics Fe reduction.

the iron reduction potential and the hydrogen evolution potential. While the reaction is substantially diffusion controlled, there are kinetic effects which are also important. As can be seen, the hydrogen evolution potential changes
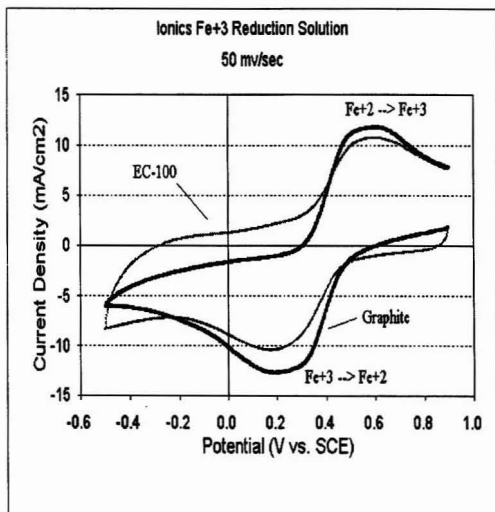
FIGURE 8 EC100 and graphite. Cyclic voltammogram with Fe$_2$(SO$_4$)$_3$.

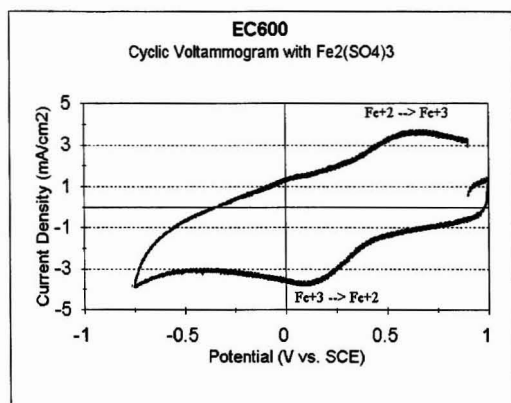**FIGURE 9** EC600. Cyclic voltammogram with Fe$_2$(SO$_4$)$_3$.

little with cathode materials. However, the iron reduction potential DOES vary significantly with the DSA coating causing the least overvoltage for this reaction. It is desirable to have the largest difference between hydrogen evolution and iron reduction. The larger this differential, the higher the current density the cathode will operate at without going into hydrogen evolution. A summary of cathode performance is shown in Table 3.

It is clear that the EC600 DSA coated titanium material was both electrochemically stable AND supported the highest current density for iron reduction before causing the electrode to go into hydrogen evolution. Therefore, finding a high surface area DSA® coated Titanium cathode became the focus of the study. Success was achieved with a woven titanium wire cloth commonly used in demisters. Eight layers of this material had a surface area of approximately 21 times its projected area. Using the limiting current density estimates, the maximum allowable current density for this structure would be approximately 37.8 mA/cm^2. Figure 10 shows the current efficiency profile obtained with 4 and 8

TABLE 3. Cathode Materials Tested

Material	H2 Evolution Potential	Fe^{+3} → Fe^{+2} Potential	Difference Between Fe & H2 Potential
AL6XN	−0.75	−0.2	0.55V
Hastalloy	−0.65	−0.375	0.275V
DSA, (EC600)	−0.75	+0.125	0.875V
Nickel	corroded		
Tin	corroded		
Silver	corroded		

layers of mist eliminator at 37.8 mA/cm^2. The effective current density for the 4 layer material is 3.3 mA/cm^2 and for the 8 layer material, 1.7 mA/cm^2. The theoretical limiting current density (Figure 2) at 750 ppm Fe^{+3} is 3 mA/cm^2. However, the 8 layer material did not reach 100% CE until an iron level of 1000 ppm was reached. At this level, the limiting CD indicates that 4 mA/cm^2 could be supported. While there is some deviation due to the estimation of the diffusion coefficient, the agreement between calculated and theoretical "limiting" current densities is good.

While efficiencies over 100% were obtained at Fe^{+3} concentrations above 1900 mg/l, with eight layers of demister material, no corrosion was observed. Average efficiency covering the Fe^{+3} concentration range of 1285 to 750 ppm was only slightly below 100%. Efficiencies over 100% are suspected to be due to variability of the analytical procedure or sampling. Runs with eight layers of demister material were also conducted with a three fold increase in catholyte velocity. No effect on efficiency was observed.

Lower Cost Cathode Developed

While the demister material provided the required surface area, a lower cost option was desired. Cathodes made from multiple layers of "heavy" expanded titanium mesh were fabricated and tested which helped further define the relationship between area and efficiency shown in Table 4. However, they did little to reduce the cost of the cathode. A cathode made of multiple layers of thin titanium mesh, coated with EC 1115, (patent pending) provided the desired area with a significant cost savings over previous options. Early results of cathode life tests were also encouraging and ongoing tests continue to show long cathode life can be expected.

TABLE 4. Current Efficiency vs. Cathode Area
(Basis: Average current efficiency between 535 and 1160 ppmFe^{+3})

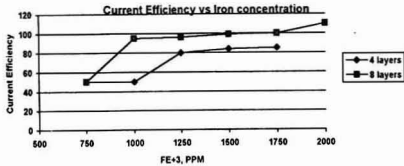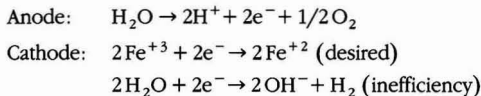| Actual/Projected Area	Current Efficiency %	Actual CD mA/cm^2
21.7	84.3	1.6
16.3	70.1	2.14
13.9	65.0	2.5
11.7	62.7	3.0
10.8	63.0	3.24

FIGURE 10 Bench efficiency vs. Fe^{+3} concentration—4 and 8 layer demister.

Based on preliminary sizing calculations it was determined that the electrolytic system would be split into two stages. The first was to run at 35 ASF (37.7 mA/sq cm) from 1285 to ~ 750 ppm Fe^{+3} at approximately 95% CE and the second was to run at 20 ASF (21.5 mA/sq cm) from 750 ppm to 285 ppm at approximately 80% current efficiency with an overall average current efficiency of greater than 85%. Figure 2 shows at 750 ppm Fe^{+3}, the estimated limiting current density was 3 mA/sq cm. Since the desired current density was 37.7 mA/sq cm between 1285 and 750 ppm, the area of the cathode had to be 12.6 times the projected electrode area. Similarly, at 285 ppm Fe^{+3} the estimated limiting current density was 1 mA/sq cm, the desired current density was 21.5 mA/sq cm, and the cathode area required was estimated to be 21.5 times the projected area.

Basic Electrolyzer Design

The principal components of the electrolyzer are shown in Figure 11. Solution rich in Fe^{+3} is passed through the cathode chamber while weak sulfuric acid is circulated through the anode chamber. Water is added to the anode compartment to replace water electrolyzed at the anode or transported through the diaphragm. Sulfuric acid is added to the anode compartment to replace acid transported through the diaphragm. The reactions are:

Anode: $H_2O \rightarrow 2H^+ + 2e^- + 1/2 O_2$

Cathode: $2Fe^{+3} + 2e^- \rightarrow 2Fe^{+2}$ (desired)

$2H_2O + 2e^- \rightarrow 2OH^- + H_2$ (inefficiency)

The anode is a dimensionally stable anode (DSA$^{®**}$) made of precious metal oxide coated titanium. The porous separator keeps Fe^{+2} away from the anode where it would be reoxidized to Fe^{+3}. It also keeps F$^-$ away from the anode which could shorten coating life. The cathode is a high surface area multi-layer DSA coated titanium. Development of an efficient cathode was the most critical aspect of the electrolytic process.

Commercial Electrolyzer Design

The electrolyzer had to meet the following design criteria:

1. Since the operating current density is low, the target cost was set at ~ $5000/m^2
2. Highly tolerant to upset conditions
3. Easily installed and maintained in the field
4. Simple to operate
5. Employ proven design principles

** *DSA is a registered trademark of Electrode Corporation.*
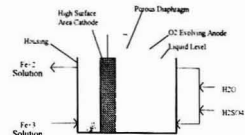
FIGURE 11 Electrolyzer components for reduction of ferric iron.

The electrolyzer design shown in Figure 12 met all these criteria. The ETC-48 electrolyzer (patent pending) consists of 48 ~ 24 × 32 inch (61 × 81 cm) cathodes, 24 anode frames and anodes, and 48 separators. Twelve and twenty-four cathode options are envisioned. This cell is an "open tank" with a hood to assist in dilution and exhaust of oxygen and hydrogen. The catholyte flows into a single open tank from the bottom through a common manifold. The flow is directed in parallel upward through each cathode set and overflows into a weir at the side of the tank. The anode frames are made of CPVC and an ELRAMIX separator is attached on each face, forming the anolyte chamber. Since ELRAMIX requires support across the 48" (122 cm) span, it is glued unto a support structure that is part of the anode frame. The cathodes are tightly fitted into the tank and compressed lightly against the ELRAMIX separator to ensure that virtually all the flow is directed through the high surface cathode. The anolyte solution is introduced into the chamber, again from a bottom manifold and discharged into a common manifold on the side of the tank. Since the cell is monopolar, all the anode and cathode current connections are made on opposite sides of the tank.

The cell is easily maintained in the field by removal of anode frames for repair or cathodes for recoating. Since the cell operates at atmospheric pressure, pressure control is unnecessary. The electrolyzer can be shipped fully assembled. Assembly in the field is also simple and requires very little special equipment since there are no heavy bulkheads to handle (as there would be in the case of a filter press cell).

Ionics ultimately installed 16 electrolyzers on skids to ensure ease of installation at the site. The skids were sized to allow them to be picked up by a standard forklift and fit into a standard sea container for shipment. A picture of a skid containing 4 electrolyzers is shown in Figure 13.

DIAMO Pilot Plant Tests

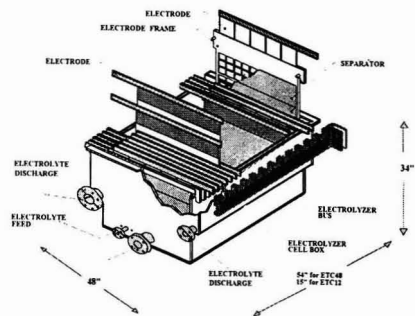To verify the selection of the cathode and separator, a

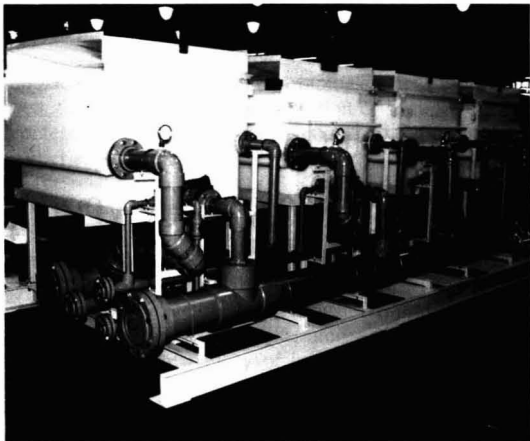**FIGURE 12** Commercial electrolyzer.

FIGURE 13 Photograph of a skid containing 4 electrolyzers.

single cell pilot electrolyzer with a half commercial size anode and cathode was fabricated and tested. Unlike the bench tests, the pilot tests were run on a once through basis at commercial design velocities to simulate the commercial process. A fine mesh cathode with a ratio of Actual/Projected area of 26 was used. "Worst case" current efficiencies obtained during pilot tests caused the average current efficiency to be slightly below the target of 85% so additional layers of fine Ti mesh were added to the cathode design raising the ratio of Actual/Projected area to 29. Final verification tests with full size commercially fabricated electrodes and separators has been successfully completed. Performance of the commercial size, single cell unit exceeded expectations.

CONCLUSIONS

A commercial ferric iron reduction electrolyzer was developed using fundamental chemical engineering principles. Limiting current density calculations were useful in predicting a relationship between current density, current efficiency, and Fe^{+3} concentration. Cyclic voltammetry was useful in selecting cathode materials for bench and pilot tests. Bench and pilot scale tests were important to characterizing the ferric iron reduction process and in selecting and verifying the commercial electrolyzer design and materials. Electrochemical reduction processes can treat high flow rate streams and have operating and economic advantages over chemical reduction processes.

Recent Work Using the ETC-48 With High Surface Area Electrodes

Subsequent to work on the reduction of iron sulfate, ELECTRODE has continued to develop additional applications for the high surface area electrode. The electrochemical destruction of organics, such as phenols, formates, and oxalates has been successfully carried out using an HSA with a DSA coating. Current densities as high as 150 Amps per square foot have been supported for the destruction of formates and oxalates. Gas and TOC analysis indicate that the organic is completely destroyed to CO_2 and water. Since the potential of the electrode during electrooxidation service is at the oxygen evolution potential, fouling is not anticipated to be the anode failure mechanism. Anodes of this type have been undergoing life-testing for 12 months with no changes in efficiency, potential, or coating loss. Work is proceeding to quantify the types of organic laden streams that will respond to this type of electrooxidation.

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Design and Economic Aspects of Activated Carbon Adsorption in Relation to the Effect of Dissolved Oxygen

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Phenol and o-c resol adsorption isotherms and columns were run under anoxic and oxic conditions. Both tests indicated that the adsorptive capacities under oxic conditions were 80%–160% higher than under anoxic conditions with very close agreement between the column and isotherm capacities. Throughput waste volumes processed in oxic columns were 70–169% higher than in anoxic columns. The economics of this oxygen-induced enhancement in sorptive capacities was addressed. Savings of 30% and 50% in operational treatment cost were estimated for o-cresol and phenol for parallel adsorber and serial schemes under oxic conditions while no differences between these two schemes in terms of the economics of this phenomenon were observed. Sensitivity analysis revealed that 15% and 30% loss of savings are incurred upon increasing the cost of GAC three-fold, for phenol and o-cresol respectively. The overall cost of oxic treatment was insensitive to the cost of oxygenation, exhibiting only a 14% increase for quadrupling the cost of oxygen. Higher oxic sorptive capacities not only results in greater savings of operational treatment costs but also less sensitivity to fluctuations in GAC and oxygenation costs.

INTRODUCTION

Granular activated carbon (GAC) is an excellent adsorbent for many of the organic contaminants present in water supplies and wastewater discharges. GAC use is frequently considered when concentrations of organic pollutants, particularly, those of the relatively non biodegradable type, must be reduced to low levels as a result of the increasingly stringent effluent standards.

Research on the effect of dissolved oxygen (DO) on the adsorption capacity of GAC for phenolics was conducted by the authors [1, 2, 3, 4] and others [5, 6, 7, 8]. Vidic et al. [6] and Nakhla et al. [1] have found that DO enhances the adsorption capacity of GAC for phenol and o-cresol. Later on Vidic et al. [7] found that the same phenomenon is valid

for ethylphenol and lake water containing natural organic matter. Abuzaid et al. [4] found that the GAC adsorption for phenol, o-cresol, 4-nitrophenol and domestic and industrial wastewater was enhanced due to DO existence. The same study showed that there was no effect in the case of aliphatic compounds. It was also suggested that the enhancement in sorptive capacity is attributed to oxygen-induced surface telomerization reactions. Abuzaid and Nakhla [3] conducted isotherm experiments for phenol and o-cresol adsorption under four different DO levels. They found that the adsorptive capacity increases with the increase in DO concentration and developed an empirical model to compute the capacities under oxic conditions when the anoxic capacities and the amount of dissolved oxygen are known. Nakhla et al. [2] have also studied the effect of pH and temperature on this enhancement phenomenon. They found that low pH favors physical adsorption while high pH promotes polymerization reactions. The optimum pH for the adsorption of phenolics under oxic conditions is pH 7. It was also found that lower temperatures favor physical adsorption and higher temperatures result in significant enhancement in the uptake under oxic conditions. Abuzaid and Nakhla [3] studied the effect of different levels of DO on the kinetics of adsorption. Their results showed that the apparent surface diffusivity coefficient for phenol in GAC decreased with increasing DO levels in the sorbate solution.

The design of fixed bed adsorbers involves an estimation of the shape of the breakthrough curve (BTC) and the appearance of the break point. Discrepancies between the isotherm capacities involved in the design and the actual column capacities were always noticed and attributed to several reasons such as continuously decreasing liquid phase adsorbate concentration in a batch [9] irreversible adsorption [9], and decline in intraparticle diffusion during the later part of breakthrough [10]. Such discrepancies have lead to erroneous designs [11]. This simultaneous adsorption-reaction uptake of phenolics may provide an explanation of the discrepancies between column and isotherm capacities.

In real applications, the DO concentration can vary ap-

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preciably. While the application of powdered activated carbon in activated sludge process can provide oxic conditions, anaerobic GAC contactors will result in complete anoxic conditions. In addition, biological activity in fixed bed adsorbers can lead to exhaustion of some of the DO content resulting in different amounts of DO in the adsorber environment.

The relatively high cost of GAC has always been an important factor affecting its use in water and wastewater treatment. The increase in the capacity attained due to DO existence may be reflected on the cost of GAC adsorption.

When the fundamental causes of this significant augmentation of sorbate uptake by activated carbon have been thoroughly researched in the literature as discussed above, there is a definite paucity of information relative to the practical implications of this phenomenon. Thus, the objective of this study is to provide further insight relative to the effect of DO on the breakthrough curves (BTC) in adsorption columns and make economic analysis of the impact of this oxygen-induced uptake enhancement phenomenon on the treatment cost.

MATERIALS AND METHODS

The 10×16 fraction (geometric mean diameter of 0.156 cm) of F-400 GAC supplied by Fisher Scientific, U.S.A. in 10×40 U.S. Mesh sizes, was used for this study. The physical properties of F-400 GAC are presented elsewhere [12]. The selected carbon size was washed several times with deionized water to remove all fines, subsequently dried at 110°C for one day, allowed to cool at room temperature for approximately 10 minutes, and finally stored in a desiccator until use.

Isotherm Tests

Single-solute stock solutions (1000 mg/l each) of phenol and o-cresol were prepared and subsequently buffered with potassium phosphate monobasic (KH_2PO_4) to maintain neutral pH. For each compound, two sets of 160-ml bottles containing identical amounts of 10×16 U.S. Mesh size activated carbon were prepared and subsequently filled with 100 ml of adsorbate solution. One set was purged with nitrogen until a zero level of DO was attained, and the bottles were quickly closed with a rubber stopper. Oxygen was purged in the other set until saturation was achieved as evidenced by a DO concentration around 30 mg/l. While such a high concentration of oxygen is unlikely to prevail in practice, it was selected to accentuate the adsorption-enhancement effect. Each set of bottles included two bottles without activated carbon to serve as blanks to check for sorbate volatilization, biodegradation, and adsorption of sorbate onto the walls of the container. All bottles were placed on a rotary shaker for a period of 14 days. It must be asserted that the relatively long equilibration time is due to the chemical reaction involved and is independent of the particle size as confirmed by Cooney and Xi [13] who demonstrated that equilibrium time for phenols on powdered activated carbon can take up to 40 days. At the end of the equilibration period, samples were withdrawn from each bottle, filtered through 0.45 μm Millipore filter paper, and analyzed for sorbate residual concentrations using Spectronic 21 spectrophotomer (Bausch and Lomb, UV-D) at a wave length of 270 nm for phenol and o-cresol.

Column Studies

Phenol and o-cresol breakthrough curves (BTCs) were obtained under oxic and anoxic conditions using 60 cm long 2.54-cm ID glass columns charged with 130 grams of activated carbon as shown in Figure 1. The influent concentrations of adsorbate were maintained at 70 mg/l for all column experiments. The feed solution to the columns was prepared using deionized water buffered at neutral pH by KH_2PO_4. The activated carbon columns were operated in an upflow mode at a flow rate of 100 ml/min corresponding to a superficial velocity of 11.8 m/h at room temperature. The anoxic runs were performed by purging the feed solution with nitrogen prior to the addition of adsorbate and keeping the solution under a head space of nitrogen. Due to the fact that 144 liters of feed solution were pumped through each column per day, it was not possible to completely strip DO and hence DO concentration was in the range of 0.1–0.4 mg/l. The oxic column experiments were performed by purging the adsorbate solution with pure oxygen until saturation was reached and a DO concentration of 30 mg/l was measured. The desired head space of oxygen was maintained by a collapsible balloon mounted on top of the feed drum.

RESULTS AND DISCUSSION

Adsorption Isotherm Equilibria

The single-solute isotherms for each case studied conformed to the Freundlich adsorption model; $q = kc^{1/n}$. The Freundlich isotherm parameters for the phenol and o-cresol isotherms are reported in Table 1. In the context of this work, the terms anoxic and oxic refer to DO concentrations of 0, and 30 mg/l respectively. Figure 2 (a, b) shows both the oxic and anoxic Freundlich isotherms for phenol and o-cresol, respectively. Two patterns pertinent to the adsorptivity of phenol and o-cresol on activated carbon should be noted. First, the oxic capacity is consistently higher than the anoxic capacity, and secondly, the difference between the oxic and anoxic sorbate uptakes increases with decreasing equilibrium concentrations. Biological activity was discounted as a reason for this enhanced sorptive capacity as no increase in inorganic carbon was observed during equilibration. Furthermore, analysis of GAC extracts from both oxic and anoxic samples revealed that the enhanced oxic sorptive capacity is attributed to oxygen-surface telomerization reactions [2, 6]. The isotherms results were discussed thoroughly by Abuzaid et al. [4], however they are presented here because they are used extensively in this work.

Column Studies

Breakthrough curves (BTC) were determined for phenol and o-cresol at room temperature and neutral pH. For each sorbate, two columns, each charged with 130 g of activated carbon and operated in an upflow mode at a superficial velocity of 0.197 m/min, were run; one under anoxic conditions and the other under oxic conditions corresponding to ~ 30 mg/l DO as described earlier.

Results of the column studies presented herein elucidate the simultaneous adsorption-surface reaction concept pertaining to the uptake of phenolic compounds in the presence of dissolved oxygen and corroborate the tremendous
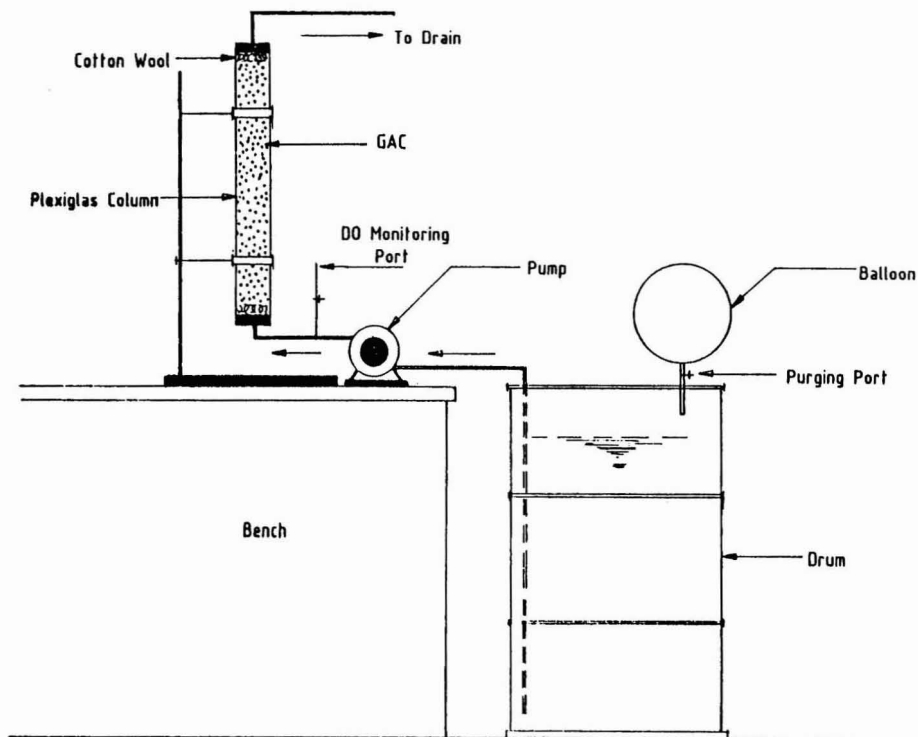
FIGURE 1 Schematic diagram of the columns setup.

impact of this phenomenon on column behavior. The breakthrough curves for phenol and o-cresol under oxic and anoxic conditions are presented in Figure 3. In order to compare between the capacities obtained from BTC's and isotherm capacities, the area above each BTC were calculated and presented with the isotherm capacities in Table 2. The oxic capacities for phenol and o-cresol were predicted using a relationship developed earlier by the authors [3] for isotherms and presented in Table 2. The relationship had the form;

$$q = q_o + M[R]^b$$

where, q and q_o are the oxic and anoxic capacities, respectively; R is the ratio of DO to GAC mass; M is the model constant (827 and 426 for phenol and o-cresol, respectively), and b is the model exponent (0.427 and 0.23 for phenol and o-cresol, respectively).

From the table it is very clear that for both phenol and o-cresol, isotherm and column capacities are very close under the pertinent DO level. The slight difference in the aforementioned capacities is thought to be due to the DO residual in the anoxic experiments which might have resulted in some polymerization reaction on the GAC surface in the adsorption column. This finding puts the question of discrepancy between isotherm capacities and column capacities reported by some researchers [9, 10, 11] to rest. It is very interesting to note that the predicted oxic capacities are close to the actual oxic column capacities which indicates that the above relationship can be used to predict the column capacities under different DO conditions given the anoxic isotherm capacity. Using the above equation, the predicted oxic capacities for phenol and o-cresol at a DO of 4 mg/l are 116.5 mg/g and 283.3 mg/g, respectively, while at a DO of 9 mg/l the aforementioned capacities for phenol and o-cresol are 128.4 mg/g and 300.3 mg/g, respectively.

TABLE 1. Freundlich Constants for Phenol and o-Cresol Isotherms

Adsorbate	DO Designation	k $[mg/g][L/mg]^{1/n}$	95% Confidence Interval [k]	1/n	95% Confidence Interval [1/n]	R^2
Phenol	anoxic	31.7	30.4–33.0	0.24	0.236–0.244	0.99
	oxic	83.5	80.6–84.8	0.18	0.167–0.193	0.97
o-Cresol	anoxic	88.6	86.9–90.3	0.19	0.182–0.198	0.96
	oxic	190.4	186.2–194.6	0.13	0.114–0.146	0.99

R^2 is the coefficient of determination.

FIGURE 2 Freundlich adsorption isotherms at 21°C and neutral pH, phenol (a) and o-cresol (b).

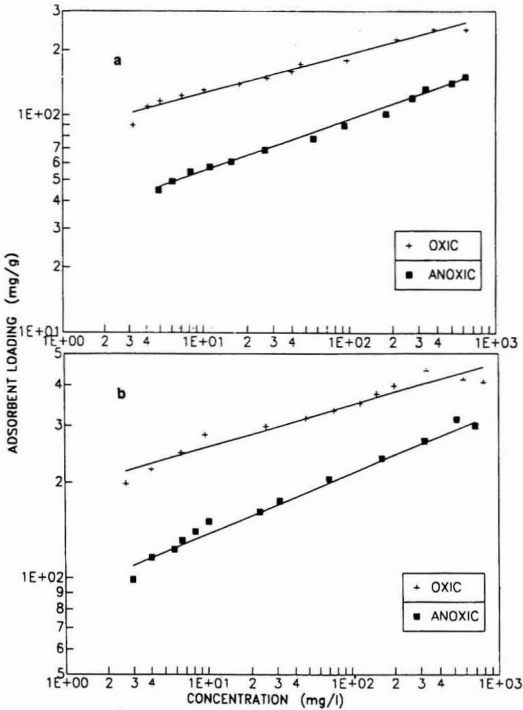**FIGURE 3** Oxic and anoxic breakthrough curves at 21°C and neutral pH, phenol (a) and o-cresol (b).

TABLE 2. Isotherm, Column and Predicted Capacities at Exhaustion for Phenol and o-Cresol

Adsorbate	DO Designation	Iso. Cap. mg/g	Col. Cap. mg/g	pred. Cap. mg/g
Phenol	anoxic	87.88	94.38	----
	oxic	179.39	171.9	158.4
o-Cresol	anoxic	198.6	207.3	----
	oxic	330.77	356.67	333.2

TABLE 3. Isotherm and Column Capacities at 50% BTC for Phenol and o-Cresol

Adsorbate	DO Designation	Iso. Cap. mg/g	Col. Cap. mg/g
Phenol	anoxic	87.88	84.6
	oxic	179.39	148.8
o-Cresol	anoxic	196.6	193.7
	oxic	330.77	295.5

In Table 3, the listed capacities are those obtained using a square wave passing through the 50% breakthrough point. The table emphasizes the findings of the previous table which really resolve the historical problem in the design of adsorption columns, namely, high discrepancies between isotherm and column capacities.

To overcome this problem, the isotherm experiment should be conducted with a DO concentration this exists in the adsorption column or the column capacity should be calculated using prediction relations [3]. Factors such as; DO content in the feed solution, configuration of the column, type of GAC, and particle size of GAC should be taken under consideration.

In many cases, the effluent criteria set by regulatory agencies governs the operation of GAC columns. Those regulations are often so stringent that the initial breakthrough in the adsorption columns is the operational criteria. This being the case, the effect of DO on breakthrough time is worth emphasizing. As shown in Figure 3, in the anoxic experiments, the initial breakthrough started after 8 hours and 36 hours for phenol and o-cresol, respectively while, for the oxic experiments, the corresponding figures were 20 hours and 62 hours. The 50% breakthrough in the anoxic columns occurred after 28 hours and 65 hours for phenol and o-cresol, respectively while for the oxic experiments, the corresponding figures were 50 hours and 100 hours. Finally, column exhaustion characterized by 95% breakthrough occurred in the anoxic column experiments after 50 hours and 93 hours for phenol and o-cresol, respectively while for the oxic experiments, the corresponding figures were 130 hours and 215 hours. These times were measured from the beginning of the experiment and give a very good indication about the tremendous additional capacity available in the column in the case of oxic conditions compared to the anoxic conditions if any particular effluent (phenolic type) standard is to be achieved.

In order to investigate the effect of oxic conditions on the treatment cost of phenol and o-cresol, the quantities of pollutants and wastewater volumes treated per kilogram of GAC were calculated at three different conditions; initial
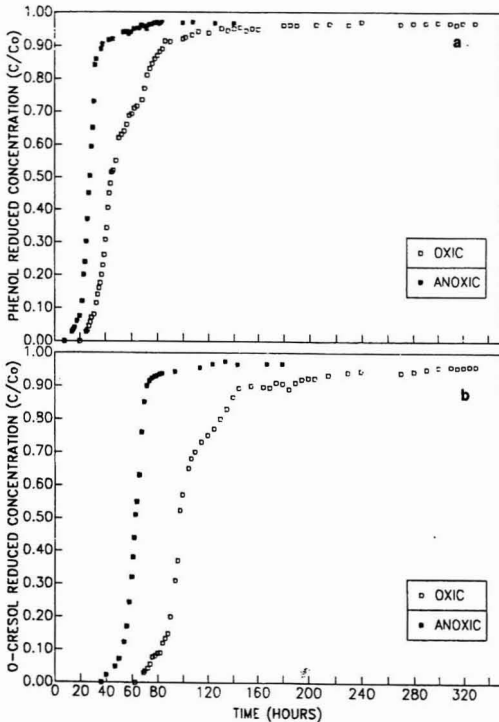
FIGURE 4 Relationship between volumes treated and percentage breakthrough, phenol (a) and o-cresol (b).
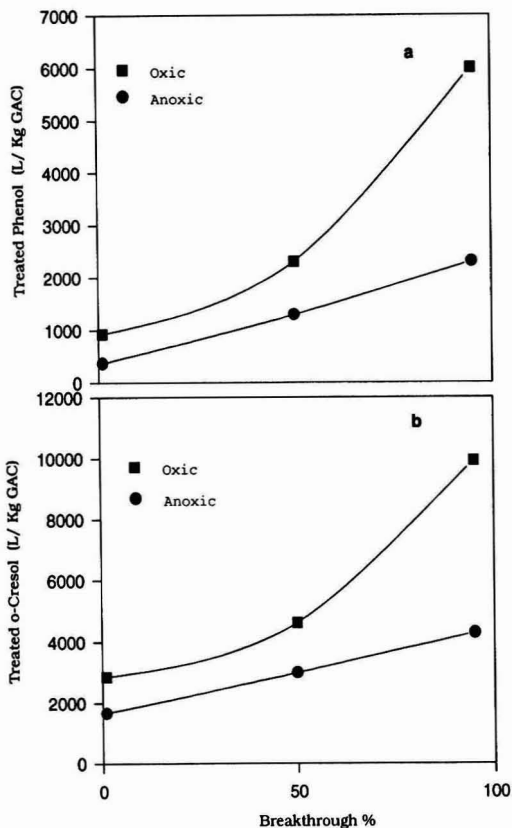

FIGURE 5 Relationship between masses removed and percentage breakthrough, phenol (a) and o-cresol (b).

breakthrough, 50% breakthrough, and 95% breakthrough. Initial breakthrough represents a single adsorber operation or parallel adsorbers wherein every adsorber has to achieve the required removal while 95% breakthrough simulates series operation in which the individual adsorbers are operated close to exhaustion. Thus the capacity referred to here is always that of the first column in the system. Figures 4 and 5 depict the variation of volumes and pollutant masses removed with percentage breakthrough. Figure 4(a) shows that under oxic conditions, the treated waste volume of phenol increases by 150% at initial breakthrough and 160% at 95% breakthrough. The corresponding numbers for o-cresol are 70% and 130%, respectively. Figure 5 indicates that the additional waste of phenol and o-cresol removed under oxic conditions is 59% and 70% at initial breakthrough and 80% and 70% at exhaustion. Thus, in terms of throughput volumes as well as pollutant loads removed, the series operation is slightly better improved than the parallel operation by the prevalence of oxic conditions. However, in terms of mass of pollutant removed, parallel operation exhibits a marginal increase over serial operation under oxic conditions. But considering that in a serial operation the enhancement referred to here is only that of the first column, it may be declared that, the overall improvement in the system is more or less the same as a single adsorber or parallel operation.
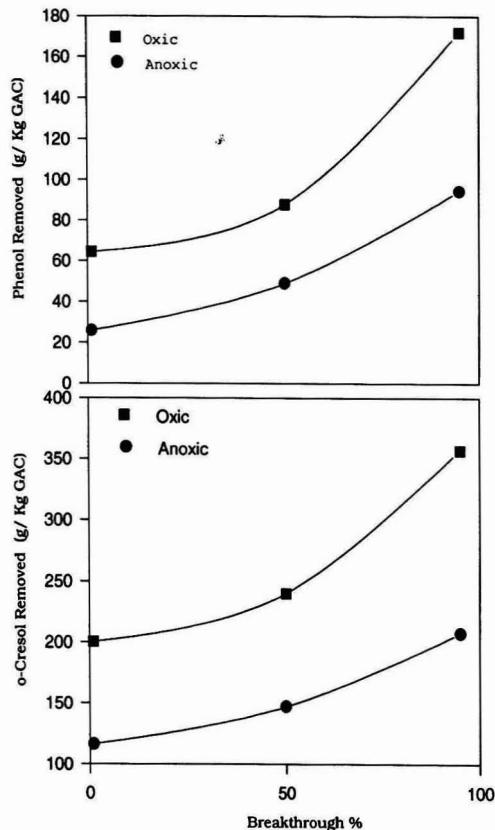
Ignoring capital costs and manpower expenses, the cost of GAC and oxygenation may be construed as the major operating treatment costs. For the economic analysis of the impact of DO on adsorption economic, actual expenses incurred during the work will be used. Procurement costs of GAC and oxygen are 4 US$/Kg and 0.67 US$/Kg, respectively. Furthermore, an efficiency of oxygen transfer during purging of roughly 7.5% was observed. Thus oxygenation costs to a DO level of 30 mg/L translates to 0.27 US$/1000 L of treated wastewater. Increased volatilization and the concomitant cost of air pollution control is impertinent to this analysis in view of the extremely low volatility of the phenols used in the study. Furthermore, the positive impact of enhanced biodegradation within the adsorber on the economics of oxic treatment was ignored due to the very short detention time in the adsorber of about 3 minutes.

Figures 6(a) and 6(b) illustrate the relationship between treatment cost and percentage breakthrough for phenol and o-cresol, respectively. It is conspicuous that oxic treatment offers substantial savings in operational costs over anoxic treatment and that the increased GAC capacity and the concomitant longer adsorber runs more than offset the oxygenation costs incurred. For phenol, oxic treatment offered a saving of about 57.5% at initial breakthrough and 46.5% at exhaustion while for o-cresol savings ranged from
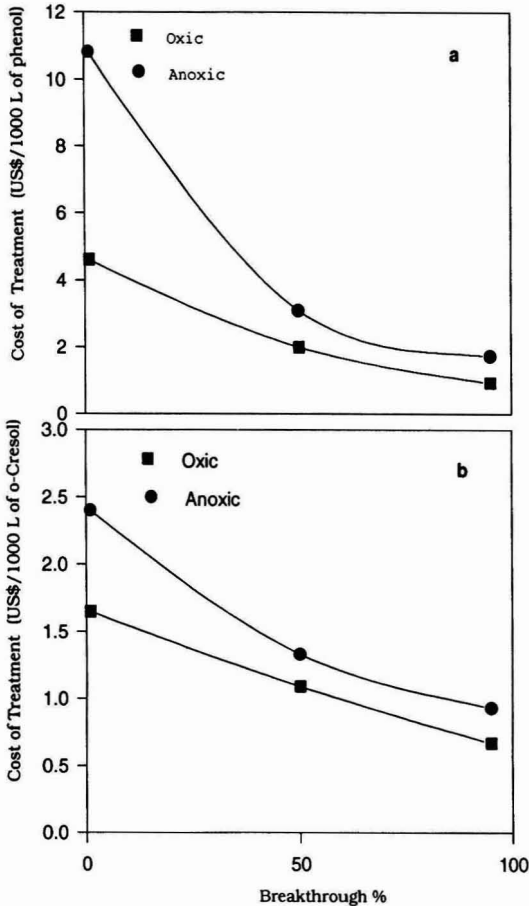
FIGURE 6 Relationship between treatment cost and percentage breakthrough, phenol (a) and o-cresol (b).

FIGURE 7 Effect of GAC cost on the cost of treatment, phenol (a) and a o-cresol (b).

29.0% at exhaustion to 31.0% at initial breakthrough. It appears therefore that irrespective of the adsorption system configuration substantial treatment cost reductions ranging from about 30% to over 50% for o-cresol and phenol, respectively, can be achieved.

The economics of activated carbon adsorption in relation to DO effects were also analyzed with respect to variations in GAC and oxygenation costs. Figures 7 and 8 illustrate the results of the sensitivity analysis undertaken. In Figure 7, the L, M, and H in the legend refer to GAC costs of 1.3, 2.7, and 4 US$/kg respectively and the oxygenation cost was maintained at 0.27 US$/1000L. The relative savings in treatment costs for 4 US$/kg GAC have already been discussed. For phenol at a GAC price of 2.7 US$/kg savings of 34% and 45% were achieved at initial breakthrough and exhaustion respectively. For the 1.3 US$/kg GAC the corresponding figures are 50% and 40%. For o-cresol at 2.7 US$/kg GAC reductions in treatment costs were 29% at initial breakthrough and 26% at exhaustion decreasing to 22% and 20% respectively for the 1.3 US$/kg GAC scenario. Generally, for a given configuration savings diminished with the decrease in GAC price, as anticipated. However, it must be noted that with 67% reduction in GAC price sav-
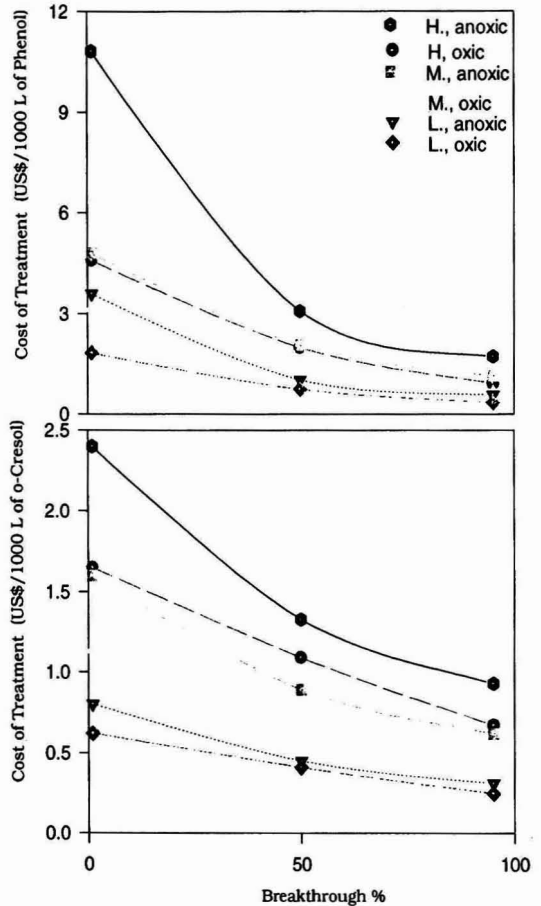
ings in phenol/treatment costs were reduced by less than 15% for both parallel and serial adsorber operations. O-cresol treatment costs were more sensitive to GAC price exhibiting some 30% reduction in savings. Furthermore, no substantial difference in terms of savings exists between the single or parallel adsorbers and serials operations.

The sensitivity of treatment costs to the cost of oxygenation is depicted in Figure 8. The price of GAC was kept constant at 2.67 US$/Kg while the cost of oxygenation was set at 0.13, 0.27 and 0.53 US$/1000L designated in the figure as L, M, H, respectively. Figure 8 shows that increasing the cost of oxygenation four-fold resulted in a constant increase of 14% in oxic treatment costs for phenol and o-cresol for different percentage breakthroughs. This is attributed to the fact that the cost of oxygenation is much lower than that of GAC and therefore represents only a minor fraction of the oxic treatment costs i.e. 5–20% of total cost. For phenol, savings compared to the anoxic costs exhibited an incremental rise of 32% at initial breakthrough and 18% at exhaustion for a four-fold decrease in oxygen cost. o-Cresol on on the other hand, showed markedly higher increases in savings varying from 39% at initial breakthrough to 50% at exhaustion. Since the incremental
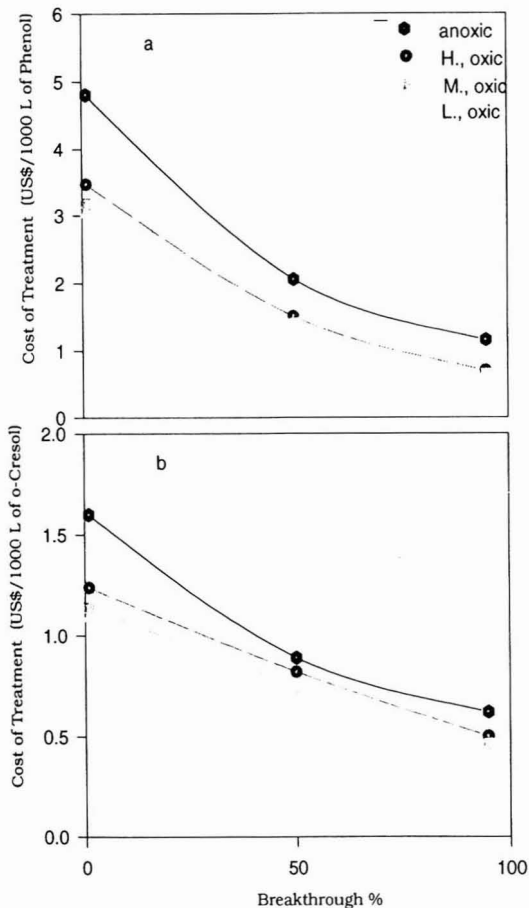
FIGURE 8 Effect of oxygenation cost on the cost of treatment, phenol (a) and o-cresol (b).

waste volumes treated for phenol were considerably higher than o-cresol, the cost of carbon saved represented a relatively bigger component of the total treatment costs savings as compared to o-cresol and thus the total savings are less sensitive to oxygenation costs. Thus as the enhancement in retention capacity increases, not only higher savings are realized but also treatment cost becomes less sensitive to both the cost of GAC and oxygenation costs.

SUMMARY AND CONCLUSIONS

Based upon the findings of this work, the following conclusions can be drawn: Column and isotherm capacities conducted under identical conditions of dissolved oxygen are in close agreement. Incremental phenol-laden waste volumes processed under oxic conditions are 150%–160% of the anoxic volumes depending on system configuration.

o-Cresol bearing waste volumes treated under oxic conditions varied from 1.7-folds to 2.3-folds anoxically treated volumes. Irrespective of the system configuration, savings in treatment costs of about 30% in the case of o-cresol and about 50% in the case of phenol can be achieved under oxic conditions. Savings in treatment costs attained under oxic conditions were generally rather insensitive to the cost of activated carbon increasing by a mere 15% for phenol and 30% for o-cresol in parallel and series operations for a 3-fold increase in carbon price. No marked differences were observed between parallel and serial configurations. Treatment costs under oxic conditions were insensitive to oxygenation cost increasing by only 14% for a four-fold increase of the latter. However, incremental savings over the anoxic treatment exhibited a rise of 17%–32%, and 39–50% for phenol and o-cresol respectively. High enhancement in sorptive capacity yielded not only larger savings in treatment costs but also less sensitive economics to changes in GAC and oxygenation costs.

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Cost-Effective Treatment of Organic Sludges in a High Rate Bioreactor

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The design and pilot testing of a deep fixed bed/attached growth high rate bioreactor (HRB) for treatment and disposal of refinery oily sludges and biosolids are described. The HRB technology is being jointly developed by Texaco Inc. and Stone & Webster Engineering Corporation to allow for the processing of refinery oily sludges, biosolids, and contaminated soils.

A key feature of the technology is its integral combination of dewatering, landfarming, and digestion operations. In essence, the technology operates as a combination of landfarm, aerobic digester, and trickling filter for semi-solids/sludges. The system provides biological degradation of wastes, and features optimal air, water and/or solids recycling, and ease of maintenance. The technology is covered by three separate patents and is particularly applicable at facilities where regulations, climatic conditions, and/or land availability limit the use of conventional land-based units.

This paper reviews current and proposed regulations pertaining to "land-banned" wastes, and presents our experience with regard to design and operation of the prototype unit.

INTRODUCTION

Landfarming was a widely used technology for the treatment of refinery oily sludges in the past. The treatment involves applying sludge to soil and tilling the soil to allow indigenous microorganisms to convert the organic fraction into carbon dioxide, water, additional microorganisms, and humic matter. Although very cost effective, landfarming has certain limitations. Landfarms are open systems and subject to climate influences. Their operation may have an effect on the soil, air, and groundwater if improperly loaded. Climate may limit landfarm operations. Cool temperatures may slow biological activity and excessive soil moisture (precipitation) may limit oxygen transfer.

The HRB technology was originally developed to allow landfarming of sludges all year around in both cold and rainy climates. As regulations changed (i.e., RCRA land ban), the HRB became an economic alternative treatment technology as an indoor and contained landfarm. The technology was specifically designed to treat refinery oily wastes (listed in Table 1) and biosolids (biological wastewater treatment sludges), while complying with the following regulations:

- Clean Air Act (CAA)
- Clean Water Act (CWA), and
- Resource Conservation and Recovery Act (RCRA)

Texaco Research and Development began development of the HRB technology in the early 1980's and has obtained three separate patents [1-3] pertaining to the process. Recently Stone & Webster Environmental Technology & Service has entered into an exclusive licensing agreement with Texaco for the HRB process, and is currently assisting Texaco in the commercialization of the technology.

REGULATORY BACKGROUND

The wastes designated as listed hazardous wastes under the Resource Conservation and Recovery Act (RCRA) that are destined for disposal must be treated prior to placement in a landfill. The treatment must be one of the processes determined by the EPA to be the Best Demonstrated Available Technology (BDAT) for that particular listed hazardous waste. For example, the EPA has designated either incineration or liquid/liquid (solvent) extraction as BDAT for the treatment of petroleum refinery K&F-wastes. An alternative treatment process may be used in lieu of the technology designated by the EPA as BDAT; however, a demonstration of BDAT equivalence must be made by the treatment facility. For this purpose, the EPA has compiled two lists of performance criteria (one for wastewaters and one for non-wastewaters) which specify the maximum concentrations of residual organics and metals for treatment of listed hazardous wastes. Table 2 lists the BDAT standards for non-wastewaters refinery listed hazardous wastes.

Unfortunately, these treatment criteria are not necessarily consistent for wastes which are typically routed to common treatment facilities. In an effort to resolve this situation, the EPA has promulgated the Universal Treatment Standards (UTS) which are intended to create a comprehensive system wherein generators of hazardous waste may select the most appropriate and cost-effective treatment method for their waste(s), provided that the selected treatment method can meet the UTS [4].

Separately, the EPA has recently promulgated regulations which affect several of the more popular disposal methods for waste activated sludge (biosolids or biosludge) generated by publicly owned treatment works (POTWs). These regulations contain strict requirements for pathogen reductions prior to placement of biosolids in a land-based

TABLE 1. RCRA Listed Refinery Hazardous Wastes

Waste No.	Description	Hazard Code
F037	Primary oil/water/solids (o/w/s) separation sludges any sludges generated from the gravitational separation of o/w/s during the storage or pretreatment of wastewaters	Toxic
F038	Secondary o/w/s separation — physical and chemical separation of o/w/s in wastewaters	Toxic
K048	Dissolved air flotation (DAF) float	Toxic
K049	Slop oil emulsion solids	Toxic
K050	Heat exchanger bundle cleaning sludge	Toxic
K051	API separator sludge	Toxic
K052	Tank bottoms (leaded)	Toxic

disposal facility [5]. In view of recent regulations and increasing cost of disposal, a process which can reduce the volume as well as stabilize the sludge would be highly beneficial.

HIGH RATE BIOREACTOR (HRB)

History of HRB

The history of the HRB now spans over a decade. In early 1980's, Texaco R&D environmental researchers identified challenges with operating landfarms in cold and rainy climates. The solution was to bring landfarming indoors.

Landfarming is the microbial process by which soil microorganisms degrade organic sludges by converting organic materials into carbon dioxide, water, humic matter, and additional microorganisms. Industrial and municipal sludge generators use landfarming to treat organic sludges, such as biosludge and oil/water separator sludge. In cold climates, microbial activity is greatly reduced when the soil temperature goes below 10°C. Effectively, landfarms are shut down during the winter months. In rainy climates, water saturated soils limit oxygen transfer, lowering the biological activity of aerobic microorganisms and creating operational difficulties for heavy equipment (tractors) to till the sludge and soil. Along the Gulf Coast, the soil temperature is suitable for year round landfarming, but rainy periods can hinder landfarming.

The proposed engineering solution to the aforementioned limitations on landfarming was an indoor landfarm enclosed by an inflatable dome and a linear system. A blower supplied air, and an interlock door permitted trac-

TABLE 2. Treatment Standards for RCRA Listed Refinery Wastes

Regulated Constituents Non-wastewaters (mg/kg)	K048	K049	K050	K051	K052	F037	F038	UTS*
Anthracene	NA	28	NA	28	NA	28	NA	3.4
Benzene	14	14	14	14	14	14	14	10
Benzo(a)anthracene	NA	NA	NA	20	NA	20	NA	3.4
Benzo(a)pyrene	12	12	12	12	12	12	12	3.4
Bis(2-ethylhexyl) phthalate	7.3	7.3	NA	7.3	NA	7.3	7.3	28
Chrysene	15	15	NA	15	NA	15	15	3.4
o-Cresol	NA	NA	6.2	NA	6.2	NA	NA	5.6
p-Cresol	NA	NA	6.2	NA	6.2	NA	NA	5.6
Di-n-butyl phthalate	3.6	NA	NA	3.6	NA	3.6	3.6	28
Ethylbenzene	14	14	14	14	14	14	14	10
Naphthalene	42	42	42	42	42	42	42	5.6
Phenanthrene	34	34	34	34	34	34	34	5.6
Phenol	3.6	3.6	3.6	3.6	3.6	3.6	3.6	6.2
Pyrene	36	36	NA	36	NA	36	36	8.2
Toluene	14	14	14	14	14	14	14	10
Xylene (total)	22	22	22	22	22	22	22	30
Cyanides (total)	1.8	1.8	1.8	1.8	1.8	1.8	1.8	590
Chromium (TCLP), mg/l	1.7	1.7	1.7	1.7	1.7	1.7	1.7	0.86
Nickel (TCLP), mg/l	0.2	0.2	0.2	0.2	0.2	0.2	0.2	5.0

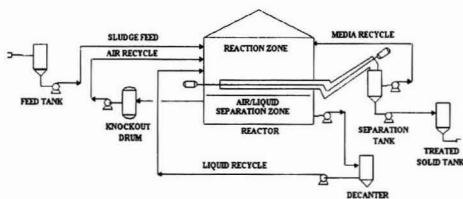NA: Not Applicable
*Universal Treatment Standards

FIGURE 1 Process flow diagram of the HRB.

tor access for sludge application and tilling. To obtain sufficient data to scale up the indoor landform design, a series of experiments were conducted over a period of a few years. Sand columns were used to determine pressure drop losses and to size a blower. A plywood reactor was built and used to determine solids and hydraulic loading rates for sludge [1].

In the late 1980's, when the land ban regulations prohibited the landfarming of oily sludges (refinery K & F-wastes) without prior treatment to remove certain constituents, a second generation of HRB experiments started. The land ban required no migration of contaminants to either groundwater or air. To accomplish these requirements and to improve operations, the technology was redesigned to be automated with computer controlled systems for air, solids recycle, sludge application, and mixing. Different media were tested to create an artificial soil for microbial attachment.

In the early 1990's, two pilot units (17 ft and 61 ft diameter reactors) were constructed and operated. The mechanical reliability of the mixing, sludge application, and air handling systems were proved. In 1994, Texaco and Stone & Webster Engineering Corporation (SWEC) entered into an agreement which grants SWEC the exclusive rights to license the patented HRB technology. With engineering assistance from SWEC, a commercial prototype unit was built with the additional feature of a solids handling system for the reactor media. The prototype unit is operating in a Gulf Coast refinery.

PROCESS DESCRIPTION

A diagram of the HRB process is shown in Figure 1. Sludges and other wastes are stored in a feed tank prior to treatment in the reactor. This tank is equipped with a mixing device and a nutrient injection system. This tank can be sparged with either air to oxygenate biosolids feed or steam to warm oily sludge which is difficult to pump. However, the process generally requires no pretreatment of wastes prior to their introduction to the process.

The heart of the process is the reactor, which is structurally an API-650, carbon steel, atmospheric storage tank; however, this tank has been fitted with an aluminum dome and with proprietary internals that functionally divide it into two operational zones. The upper portion of the reactor is the reaction zone, where sludge is dewatered and solids are retained by the reactor bed media. The organic fraction of the solids is degraded by microbes. One of these proprietary internals is a mixing device which "equalizes" the sludge loading and prevents the formation of anaerobic "dead spots" among the wastes, biological organisms, and support media that together comprise the reactor "bed".

The lower portion of the reactor functions as an air/liquid separation zone; this zone is separated from the reaction zone by an underdrain layer that precludes passage of the support media, while facilitating the separation of air and liquids from solids.

Treated wastes, microbes and support media may be periodically and/or continuously removed from the reaction zone by a solid conveying system that transports the reactor bed contents to the adjacent Separation Tank, which has been equipped with a cone bottom to facilitate this operation. This tank is also used to remove treated solids from the process for testing and storage pending transport to an off-site disposal facility. One part of the conveying system is used to return wastes, microbes, and media to the reaction zone, thereby controlling solids retention time and the population of microorganisms in the reactor bed. Recycling the media minimizes the amount of solids ultimately sent to disposal.

The reactor effluent is pumped to another adjacent cone-bottom tank, the "Decanter." Decanted liquid is discharged directly to POTWs, or routed to the facility wastewater treatment, depending upon configurations and permit requirements. Alternatively, it can be recycled to adjust moisture content in the reactor bed. Solids separated in the conical section of the decanter are either recycled to the feed tank for further treatment or disposed of once all the necessary discharge requirements have been met.

Air is circulated through the reactor by means of the liquid knockout drum and blower. The centrifugal blower supplies the necessary amount of air flow to sustain the microbial (aerobic) oxidation of the organic matter in the wastes. Because of depletion of oxygen during the biological oxidation, an oxygen sensor is installed to monitor the O_2 content to determine how much fresh air needs to be introduced into the air circulation loop to maintain aerobic conditions within the reactor. To balance the intake of fresh air into the system, a slipstream of the circulated air is vented through an emission control device, such as an activated carbon filter, to trap any volatile organic compounds (VOCs) that may be present in the air. Since air is recirculated back into the reactor (until O_2 depletes to low levels), the reactor acts as a biofilter to degrade VOCs in the air. Initial results indicate that VOC emissions are less than 1 ppmv during biosolids treatment. Normally air is circulated from top to bottom in the reactor to assist in dewatering the sludge, but, if desired, the normal downflow pattern of air recirculation can be reversed to dry the lower portion of the reactor bed.

HRB FEATURES

The HRB process is uniquely capable of simultaneously dewatering and biologically degrading either hazardous oily wastes or biosolids with an enclosed and controlled environment. In contrast to conventional landfarming, the process is completely isolated from the environment and exerts strict controls on all inputs, the physical-chemical environment, and the fate of the transformed waste products. In addition to being protected from precipitation and other environment intrusions, each of the system components may be heated to keep operating temperatures within preferred ranges. As a consequence, not only can the system be operated twelve months of the year in inclement

weather, but also the optimum temperatures can be maintained to maximize biological activity.

The HRB utilizes a "solid-phase" process rather than a slurry process. Compared to slurry-phase biological treatment, the process differs in terms of aeration, agitation, and solids content. The HRB requires less energy to operate than a slurry reactor, because the mixer does not have to keep the suspension in solution; and because oxygen transfer is through a solid matrix instead of a liquid matrix. During the operation of the HRB system, pH, temperature, nutrient concentrations, and moisture content are maintained within ranges conducive to microbial activity. If necessary, highly concentrated waste can be mixed with less concentrated waste to reduce the contaminant concentrations to levels that would not be toxic to the microorganisms. Depending on the nature of contaminants, waste characteristics, and a number of other site-specific factors, the system can be modified to increase the degradation rate and throughput.

The system is equipped with a data acquisition and control system to make the process easily controllable and simple to operate. The process can be operated either in a batch or a continuous mode. The prototype unit is typically run by one operator on a 5-day, day-shift schedule, plus minimal attention during the off-shifts and weekends.

TREATMENT OF BIOSOLIDS

For the treatment of biosolids, the HRB process combines sand bed dewatering, landfarming, and aerobic digestion. In aerobic digestion, as the supply of substrate (food) is depleted, the microorganisms begin to degrade their own protoplasm to generate energy for maintenance as shown below:

$$C_5H_7NO_2 + 7O_2 \Rightarrow 5CO_2 + NO_3^- + 3H_2O + H^+ \quad (1)$$
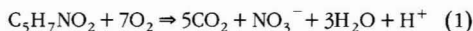
As the sludge digestion progresses, pH will drop if the alkalinity of the sludge/liquid/soil mixture is not sufficient to buffer the solution. In reality, the organic fraction (only about 70 to 80 percent of the microbial mass) can be oxidized; the remaining 20 to 30 percent is composed of non-degradable and inorganic components. A major objective of aerobic digestion is to reduce the mass of biosolids for disposal. The rate of degradation of volatile suspended solids (VSS), a degradable portion of microbial mass, can be represented by a first-order reaction:

$$dC_{vss}/dt = -K_d C_{vss} \quad (2)$$

K_d = reaction-rate constant
C_{vss} = concentration of biodegradable volatile suspended solids

The reaction rate K_d is a function of the sludge type, temperature, and solids concentration. The degradation rate is influenced by several factors; one of the important factors is concentration of VSS in the reactor.

The HRB technology has inherent advantages over a conventional aerobic digester. The reactor is smaller and less expensive than a digester with the same VSS residence time because the free water is not retained in the reactor. In addition, the biomass concentration is higher, so the reaction rate per unit volume of reactor is higher. Other advantages of the HRB process are the continuous flushing of
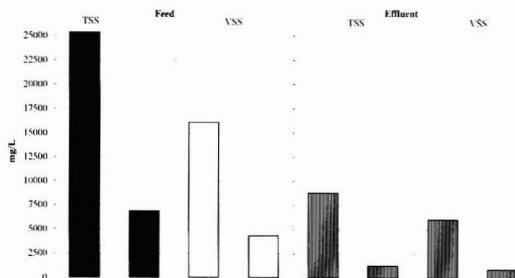

FIGURE 2 Range of solids content in the feed and effluent.

the "stored" sludge in the reactor and the removal of soluble end products such as ammonia and nitrate, which may build up and become toxic to the remaining microorganisms and limit the biodegradability. Additionally, unlike composting, HRB reactor bed never gets so dry that the growth and metabolism of microorganisms responsible for biodegradation is not inhibited.

The testing of biosolids began in August of 1994. The prototype unit ran on biosolids from a refinery activated sludge treatment unit (ASTU) for seven months.

The solids content of the feed varied from a low of 5,000 to 10,000 mg/l of TSS (total suspended solids) from the clarifier to a high of 20,000 to 30,000 mg/l of TSS from the thickener. The process did not require any pretreatment of feed. Figure 2 shows the range of solids content in the feed and effluent from the process. The excess free water in the feed was drained under gravity, while biosolids (microbial mass) were retained in the reaction zone.

The solids content in the reactor increased during the startup. However, the solids content remained fairly constant or stable once the process reached the equilibrium as shown in Figure 3. This is indicative of the fact that even at the higher loading rates, the reactor was able to biodegrade an increased amount of solids in response to what it was fed. It is important to minimize the accumulation of inorganics in the reactor because they will reduce the effective treatment volume, and because the higher concentration of inorganics may inhibit the biological process.

An important parameter, oxygen uptake rate (OUR), was measured along with other parameters such as pH, conductivity, nitrate, total petroleum hydrocarbons, and metals. The OUR is a measure of the biological activity. Oxygen uptake is valuable for HRB operations when combined with VSS data. The combination of the OUR with the concentration of VSS is termed "specific oxygen-uptake
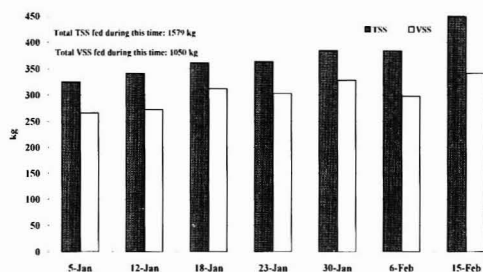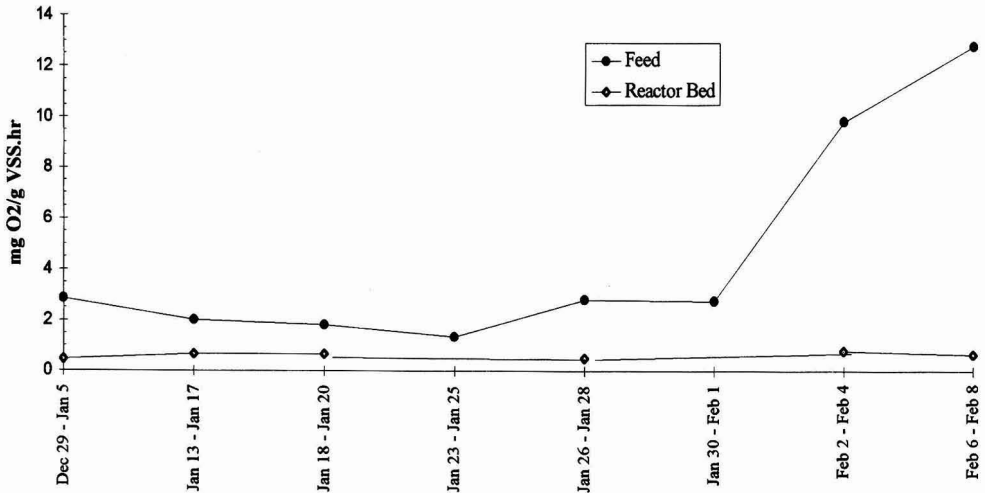

FIGURE 3 Solids content in the reactor.

FIGURE 4 Comparison of SOUR.

rate" (SOUR). SOUR is a measure of the respiration rate. The SOUR values indicate the degree of sludge treatment: the lower the value (< 1.0 mg O_2/gm VSS/hr), the better stabilized or treated the sludge is. Figure 4 demonstrates the ability of the HRB process to lower the SOUR of the incoming feed from an average of 3–4 mg O_2/gm VSS/hr to 0.5–0.7 mg O_2/gm VSS/hr.

The overall performance of the unit is summarized in Table 3. The overall efficiency of the process ranged from 45 to 60 wt.% when loading rates were increased by six fold from 0.5 to 3.2 kg of solids/m^3 of reactor/day. The high biosolids loading rates make the HRB process economically attractive compared to other treatment technologies (digestion and composting).

Lessons learned from the operation of prototype unit are summarized below:

- The HRB process successfully treated biosolids (based on VSS and SOUR reductions) even at low temperatures (7 to 12°C) in the winter.
- The reactor stirring mechanism has proven itself to be mechanically reliable.
- The artificial bed media showed no signs of wear.
- The scale-up and design process parameters obtained from bench-scale testing were confirmed during prototype operation.
- The process is tolerant of upsets, including interruption to feeding and mixing, excursions in total feed as well as solids concentrations, and temporary interruptions of airflow.
- The equipment for removing and handling the reactor solids and media is functional. Opportunities to increase both efficiency and reliability were identified.

TABLE 3. Performance Data

Loading Rate (kg of solids/m^3-day)	0.5–3.2
Overall VSS Reduction (wt.%)	45–60

TREATMENT OF OILY SLUDGES

For the treatment of oily sludges, the HRB process is similar to HRB biosolids treatment. It dewaters and mixes the oily sludges with an inert and non-friable bulking agent in the presence of an active microbial population. Forced air is passed through the reaction mixture to assist in the removal of excess (free) water and to provide sufficient oxygen for biodegradation. The most important parameter for the design and operation of HRB process to treat oily sludges is the loading of petroleum hydrocarbons. With its controlled environment, the HRB can treat a significantly higher amount of petroleum hydrocarbons (quantity of sludge) per volume basis compared to conventional landfarming.

The main goal for treatment is to reduce the concentration of specific petroleum hydrocarbons present in oily sludges to meet the UTS for refinery hazardous wastes. Some of the regulated constituents, such as polynuclear aromatic hydrocarbons (PAHs), in the sludge are recalcitrant and may require longer treatment time for degradation than short chain hydrocarbons [6]. In bench-scale testing, the HRB technology has proven its effectiveness as a treatment process for RCRA hazardous wastes (refinery K & F-wastes) by producing treated solids which contain organic residuals below BDAT limits established by the EPA. In addition, metals contained within the treated sludge are expected to be naturally stabilized due to the chelating effects of the biological activity. As a result, treated solids are generally suited for direct disposal in a landfill. Presently, the HRB prototype unit is testing oily sludges to collect the information for the design of a commercial unit and to determine treatment efficiencies relative to UTS.

ECONOMIC DATA

The results from bench-scale studies and prototype testing have demonstrated that the HRB process is a cost-effective, regulatory compliant alternative for the treatment of a wide variety of solid wastes (biosolids and oily sludges). Results of some of the bench-scale studies are discussed in

U.S. Patent 4,668,388 [1]. Texaco and Stone & Webster have combined forces to continue assessing the performance of the HRB through exhaustive testing of the full-scale prototype unit.

Data compiled during the design and the demonstration phases indicate that treatment costs for biosolids and oily sludges vary from $100–$450 per ton of dry solids in the feed. The cost is highly dependent on the site conditions. These figures make the technology very competitive, particularly in comparison to either thermal or chemical processes.

BENEFITS AND ADVANTAGES

The benefits of the HRB process are as follows:

- The self-contained system is isolated from the environment. Since it is housed within tanks and can operate with a reaction bed depth measured in meters (1.5 to 3 m), the process requires significantly less surface area than a traditional landfarm with 15 to 30 centimeters of zone of incorporation (ZOI). The HRB reactor bed is all ZOI.
- The HRB process control and monitoring systems require minimal operator attention.
- The system operates at normal temperatures and pressure. This keeps cost and safety issues to a minimum compared to technologies using pressure vessels and high temperatures. Year round operation is sustainable, independent of the climate.
- No exotic alloys or other materials are used for construction; virtually all components are constructed of either carbon steel or PVC. Materials are inexpensive and easy to modify/expand if required.
- The process combines high solids loading rates with low capital and operating costs. The process is expected to achieve significant reductions in waste mobility, toxicity, and volume.

SUMMARY

The HRB process can treat refinery oily sludge as well as industrial and municipal biosolids. To date, a total of three process patents have been issued on HRB technology. The HRB prototype unit has treated refinery biosolids successfully and is presently treating an oily sludge. Bench-scale HRBs met BDAT standards for oily sludges.

Using the full-scale prototype unit at a Gulf Coast refinery, Texaco and Stone & Webster are continuing with demonstration of the HRB process in order to bring it into full commercial readiness.

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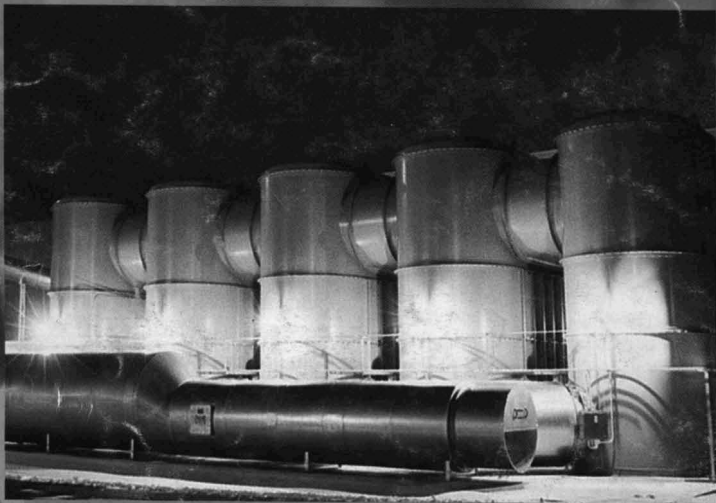
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