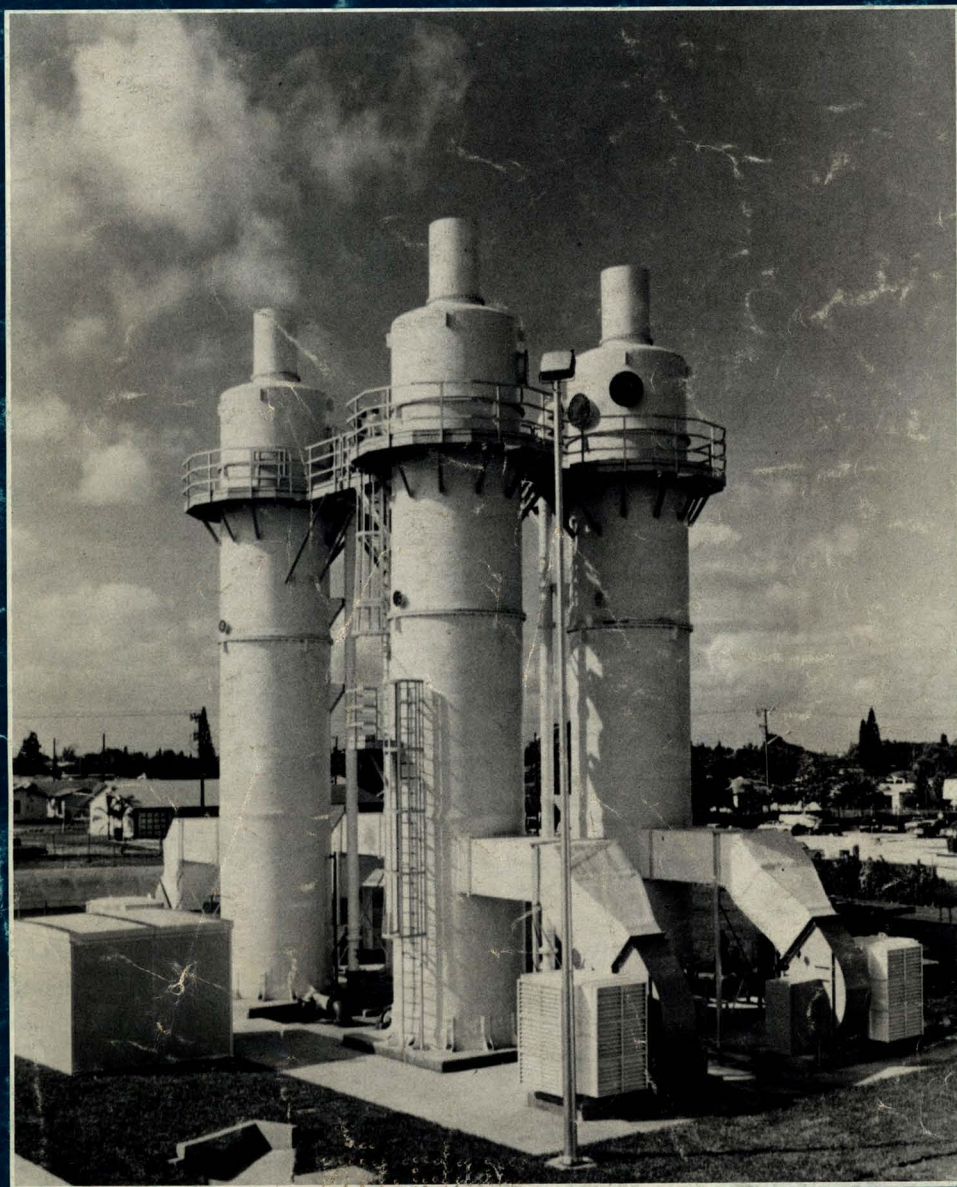


MAY 1990

ENVIRONMENTAL PROGRESS



Fiber glass reinforced plastic scrubbing towers in Delray Beach, Florida.
Photo courtesy of Industrial Plastic Systems Inc., Lakeland, Florida.

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Environmental Progress is a publication of the American Institute of Chemical Engineers. It will deal with multi-faceted aspects of the pollution problem. It will provide thorough coverage of abatement, control, and containment of effluents and emissions within compliance standards. Papers will cover all aspects including water, air, liquid and solid wastes. Progress and technological advances vital to the environmental engineer will be reported.

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The Political Dilemma of Recognizing Necessary and Available Industrial/Hazardous Waste Solutions

T. L. Kovacic

The dilemma confronting politicians today, regarding our nation's industrial/hazardous waste problem, is recognizing existing and available solutions. Due to the overwhelming amount of misinformation, emotion, and mis-directed (sometimes self-serving) motives, solutions are being confused with problems.

While we as a nation have made some progress in reducing and managing our industrial wastes, future progress is being seriously stifled largely due to NIMBY (Not In My Backyard) patrols and media-seeking activists. Unfortunately, these mis-directed, very vocal protest groups, have, regrettably, prevented necessary environmental cleanup progress while allowing serious environmental degradation to continue. This problem will only continue until the public becomes aware of the real issues and politicians decide to listen to authentic environmentalists. It is rare to find a politician who is informed enough, and/or has courage enough to take a position in support of a necessary industrial/hazardous waste secure landfill. Why? Because of the enormous pressure that, inevitably, comes from local activists who either lead a local NIMBY group, or refer to themselves as environmentalists preventing another Love Canal.

For every safe and necessary landfill there are thousands, if not tens of thousands, of old dumps that should receive attention. Today, there are only 23 commercially secure industrial/hazardous landfills in the country. There should be approximately 230 secure landfills. For every day's delay in siting and constructing additional secure landfills, tens of thousands of tons of existing industrial waste in old dumps continues to contaminate the environment. Recently generated waste is improperly disposed of.

The local NIMBY mentality has now escalated to statewide proportions. The state of Alabama recently enacted legislation aimed at curbing the flow of industrial/hazardous waste into the state. The Alabama legislation seeks to prevent incoming waste from any state that has not assumed their responsibility in treating or disposing of their own waste. Assuming that the intent of the Alabama legislation is to encourage, if not force, other states to recognize the problem, it would appear such action might have a positive environmental impact. Unfortunately, one can also assume that such legislation is the result of local political pressure, surely furnishing a model for national state-by-state copycat legislation. What positive problem recognition might be gained will more than likely be offset by improper/illegal disposal and threatened industrial growth. Similar copycat legislation (not unexpectantly) was just recently introduced in Ohio.

It is interesting to consider the proposed Ohio legislation, in light of the fact that Ohio exports about as much hazardous waste as it imports. It is even more interesting, when you consider that the waste Ohio exports typically consists of relatively more hazardous wastes than it imports. Therefore, if Ohio is eventually forced to keep all of its own hazardous waste within its borders, the state would be unable to dispose of it.

Until available environmental solutions like secure landfill cells are politically not only recognized—but endorsed—our environment, industrial growth, and economic future will all suffer. For environmental and economic reasons we, as a society, must strongly



Reproduced from *Waste Age*, March 1990.
 © National Solid Waste Management Assoc., Washington, D.C.

support recycling, waste minimization, and beneficial reuse. We must, however, just as strongly support the safe and proper disposal for that fraction of our waste, or final residue, that must be disposed of. We must face reality, and support politicians who face reality, because the activists and NIMBY patrols are most assuredly going to produce environmental and economic disruption if they are not politically challenged.

As previously mentioned, the NIMBY mentality has now grown from city to state proportions. Perhaps the next phase is a national ban on constructing secure landfill cells. The inevitable generation of industrial waste can then be eliminated or ignored immediately, by either closing down any industry that produces waste or ignoring environmental protection and allowing indiscriminate disposal. Obviously, both of these alternatives are not real options—or are they?

The land disposal restrictions that have been evolving as a result of RCRA objectives have definitely affected both industry and disposal facilities, and will eventually and positively benefit the environment. But if there is no place to eventually dispose of residual waste safely and in an environmentally sound manner, where is it finally going to be deposited? The March, 1990 cover of *Waste Age* humorously, but yet appropriately, captures the situation.

The problem or dilemma is not going to disappear. It is time that politicians recognize the severity of our industrial waste problem and endorse proper and available solutions. It is time that *real* environmentalists begin to demand as much media and political attention as the activists. It is time that our true, and much needed, concern for the environment take priority over mis-information and self-serving interests.

Finally, it is time for *real* political leaders to assume their responsibility, and help solve the nation's industrial waste disposal dilemma, and help the public understand the difference between industrial waste problems and solutions.

T. L. Kovacic is president of Envirosafe Services of Ohio, Inc., an industrial/hazardous waste management facility in Toledo, Ohio. He previously served as Toledo's director of public utilities from 1982-1989 before accepting his current position. Mr. Kovacic holds a bachelors degree in chemistry/geology and a masters degree in geochemistry, both from Bowling Green State University.

Washington Environmental Newsletter

EPA Expands Technology Innovation Efforts

The Technology Innovative Office of EPA's Office of Solid Waste and Emergency Response is looking for ways to increase applications of innovative treatment technology by government and industry to contaminated waste sites, soils and groundwater. Increased usage will be accomplished through the removal of regulatory and institutional impediments and the provision of richer technology and market information to targeted audiences of federal agencies, states, consulting engineering firms, responsible parties, technology developers and the investment community. The scope of the mission of the Technology Innovation Office (TIO) extends to Superfund sites, corrective action sites under RCRA and underground storage tank cleanups. By contrast TIO is not a focus for EPA interest in treatment technologies for industrial or municipal waste *streams*, for recycling or for waste minimization. Other offices address these special interests.

For purposes of remediation, innovative technologies do *not* include rotary kiln incineration, conventional stabilization or other methods where sufficient performance and cost information are available. Land disposal technologies are also not included within the scope of TIO's interests. *Innovation in thermal methods, bioremediation, physical/chemical techniques and groundwater extraction and treatment technologies is of principal interest.* Innovative monitoring methods are of interest, but are a secondary priority.

Approach—TIO will influence the increased use of innovative technologies by working with and through knowledgeable individuals and groups both inside and outside EPA. TIO accomplishes its internal mission as a partner with other waste program offices and EPA's Office of Research & Development.

Within the agency, TIO exercises policy leadership and sets expectations, assists in the implementation of demonstrations of technologies under the Superfund Innovative Technology Evaluation (SITE) program, analyzes trends in agency technology decisions, helps screen technology types and vendors, and serves as a champion for agency attention to innovative technologies. A collateral objective for TIO is brokering the transfer of information on the cost and performance of all alternative technologies for waste remediation.

Beyond EPA, TIO is engaging the principal stakeholders in innovative site remediation—consulting engineers, responsible parties, technology vendors, venture capitalists, universities, States and professional associations (AIChE is included)—in the challenge to increase the use of innovative technologies. This joint work involves both identifying mutual interests between and among these parties and EPA waste programs and then devising mechanisms to act upon them. Because EPA is a member of the family of Federal agencies interested in lower cost, innovative treatment technologies, TIO is establishing a Federal Remediation Technologies Roundtable to maximize the sharing of available Federal experience.

For more information on TIO's program, contact Dr. Martin Siegel at the address shown at the bottom of this page.

*This material was prepared by AIChE's Washington Representative, Siegel • Houston & Associates, Inc.
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EPA Reports on Status of Technologies Aimed at Acid Rain Control

The U.S. Environmental Protection Agency (EPA) recently announced the successful demonstration of the low cost LIMB retrofit process capable of 60% SO₂ removal. EPA has also successfully pilot tested the ADVACATE process, a retrofit process capable of greater than 90% SO₂ control with costs projected at less than half that of conventional flue gas desulfurization (FGD).

EPA recently briefed the electric utility industry on the status of technology it has been developing and demonstrating for reducing acid rain

precursors, sulfur dioxide (SO₂) and nitrogen oxides (NO_x), from existing coal-fired utility boilers. The retrofit technologies discussed included Limestone Injection Multistage Burners (LIMB) and ADVACATE (advanced silicate). Results from EPA's recent full-scale LIMB demonstration at the Ohio Edison Company's Edgewater Unit 4 in Lorain, Ohio, highlighted the meeting held at EPA's Environmental Research Center, Research Triangle Park, North Carolina.

The full-scale LIMB tests at Edgewater showed that over 60% SO₂ re-

moval and about 50% NO_x reduction is achievable. Also discussed were results from the recent combined LIMB/ADVACATE field evaluation at Edgewater, in which more than 90% SO₂ was removed. Additionally, plans for the next LIMB, and possibly LIMB/ADVACATE, demonstration at Virginia Power Company's Yorktown, Virginia were presented.

Further details may be obtained by writing to the U.S. EPA, Air and Energy Engineering Research Laboratory, Mail Drop 60, Research Triangle Park, North Carolina 27711.

CMA Opposes Additional Environmental Taxes on U.S. Businesses

A chemical industry spokesman recently told a Congressional panel that imposing additional environmental taxes on U.S. businesses would damage their international competitiveness and would lead some manufacturers to relocate production capacity overseas.

"The chemical industry opposes new and industry-specific taxes and especially opposes taxes that would . . . impair the competitiveness of U.S.-based manufacturing," Sean T. Crimmins, a spokesman for the Chemical Manufacturers Association, told the House Ways and Means Committee. The committee is considering legislation to enact new environmental taxes.

Crimmins, vice president and general tax counsel at Ashland Oil, Inc., said the U.S. chemical industry already is subject to a 37 percent effective tax rate, plus excise taxes paid on certain chemicals to the Superfund and on chlorofluorocarbons (CFCs) production. The industry also pays waterway users and petroleum feedstock taxes, he said.

Crimmins said a survey of CMA's membership, which comprises over 90 percent of U.S. chemical production capacity, shows that industry expects to spend "well over \$3 billion on environmental controls. "That amount does not include additional costs that may arise from pending revisions to the Clean Air Act."

He also said that "ideally" clean-up programs that repair existing environmental damage should be paid through general revenue funds. Beyond that, he advocated that a broad-based tax program, such as the Superfund's Corporate Environmental Tax, should be adopted.

Crimmins told the committee that the U.S. should continue to be an environmental leader. Paying for a better environment, he added, is largely dependent on maintaining a competitive manufacturing sector. Crimmins added "Tax policies that create additional disadvantages for U.S.-based production . . . will increase the overall cost to the U.S. economy of meeting these environmental goals."

Book Reviews

Hazardous Waste: Detection, Control, Treatment; Parts A and B, by Richard Abbou, Elsevier Science Publishing Company, Inc., New York, NY, (1988) 1838 pages [ISBN No.: 0-444-42985-9 (Part A)] [ISBN No.: 0-444-42986-7 (Part B)] U.S. List Price: \$460.50.

The field of hazardous wastes is concerned with many complex issues, and complicated scientific and technical problems. Concerns exist for the proper treatment and management of hazardous wastes, the toxicity and degree of hazard for the waste, ultimate disposal of the waste, and monitoring at the disposal site. This book addresses such concerns; the book represents the Proceedings of the World Congress on Hazardous Waste, held in Budapest, Hungary, on October 25-31, 1987. These two books (Parts A and B) contain a total of 162 papers (83 in Part A and 79 in Part B) which were presented at the conference. The conference attracted 350 people from 39 countries, indicating the international attention being devoted to the issue of hazardous wastes.

The two-volume set is divided into seven basic sections. Part A begins with Section 1 which contains 14 papers concerned with the definition of hazardous waste, including classification, risk assessment, proper management practices, and the transport of hazardous wastes. Section 2, containing 30 papers, is concerned with the present status and trends in legislation and regulation. Included in this section are papers devoted to waste reduction/waste minimization, hazardous waste management and control, educational training, and hazardous waste disposal.

Section 3 contains 11 papers and is involved with data collection, analysis, and control systems. Papers are included in this section which address sampling systems, chemical equilibrium modeling, modeling of technological processes, laboratory and field validation, leaching procedures, tracking of hazardous wastes, improved monitoring techniques, and hazardous waste identi-

fication using elemental analysis. Section 4, containing 28 papers, is concerned with ecological impacts. Papers address such topics as new decontamination techniques, waste classification, analysis of soil toxicity, soil microbiological properties, hazardous assessment procedures and effects of various hazardous wastes in the environment (air, water, and soil).

Part B begins with Section 5 which contains 16 papers in the area of health impacts. These papers are concerned with sampling, testing, and evaluation procedures, public health effects, chemical analyses for assessment and evaluation for human exposures, genetic activity, occupational health and safety rules, neurotoxicological studies, and other similar topics.

Section 6 is a large section containing 53 papers in the area of technological state-of-the-art. Papers are included which are concerned with multimedia environmental pollution control; regional hazardous waste management approaches; collection and destruction of hazardous wastes; solvent recovery; recycling, reuse, recovery, and reutilization; incineration/emissions control; treatment of PCB-containing wastes; liners for containment of hazardous wastes; solidification/stabilization techniques; chemical fixation; neutralization; biological treatment; precipitation/flotation for removal of heavy metals; and aquifer restoration.

Section 7, dealing with economic and psycho-sociological aspects, contains 10 papers. These papers address such topics as minimizing hazardous waste site clean-up costs, hazardous waste incineration at sea, citizens groups concerned about hazardous wastes, and problems associated with various hazardous wastes. The book concludes with a short summary of the panel discussions from the conference.

The two-volume book points out that the single most serious, global environmental problem for the 1980s and 1990s is that of hazardous wastes affecting soil, water, and air, and finally endangering human health. The harmful effects caused

by improper management of hazardous wastes are not confined to national boundaries. The generation, treatment, and disposal/recycling of hazardous wastes is related to the economic and ecological processes in all countries, pointing out the need for efficient international cooperation.

This book is very interdisciplinary and international in scope. The book would be an extremely valuable resource for people concerned with hazardous wastes, including plant managers, environmental and chemical engineers, university researchers, regulatory personnel, governmental agencies, and consultants.

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In Situ Immobilization of Heavy-Metal-Contaminated Soils, by G. Czupyrna, A. I. MacLeon, R. D. Levy, and H. Gold, authors/editor, Noyes Data Corporation, Park Ridge, NJ, (1989). 155 pages [ISBN No. 0-8155-1219-8] U.S. List Price: \$39.00

The disposal of waste streams containing heavy metals has oftentimes led to problems with contamination of both soil and groundwater. Percolation of water into the subsurface environment can result in the solubilization and mobilization of heavy metals. This book reports on the evaluation of various treatment chemicals for immobilizing heavy-metal-contaminated soils. Currently available technologies for treating contaminated soils include excavation of contaminated soils for drumming or soil washing and subsequent treatment of the washwater using pH adjustment and precipitation of the heavy metals. *In situ* immobilization could avoid the requirement of excavating the soils or pumping

the groundwater for on-site treatment. This process prevents the hydrolysis of the metals and the desorption of the metals from varying conditions in the soil (such as low pH and shifting oxidation/reduction potential) which tend to solubilize the metals. Twenty-five (25) chemical additives were screened for their ability to react with heavy metals in soils.

The book is divided into nine sections and contains two appendices. The book begins with an Executive Summary which overviews the test program, summarizes the leaching test results, provides a cost analysis, and offers recommendations.

The book then presents a brief Introduction section which puts forth the objectives of the program, background, and scope of the report. Section 2 addresses the soil characteristics in terms of particle size, cation attraction affinity, adsorption potential, precipitation of metals, interactions of soil and the contaminant metals, soil collection, and soil analyses.

The treatment chemical additives, including standard cation exchange resins, chelate ion exchange resins, metal scavengers, clays, molecular sieves, greensand, hydrated lime, silylated silica gel, insoluble starch xanthate, Metal Sorb-7, and ferrous sulfate are all addressed in Section 3. Section 4 describes the test apparatus and analytical techniques employed in this evaluation.

Section 5 describes the test approach and results in terms of batch screenings, dynamic flow column tests, long-term stability column tests, and hazardous waste simulation tests. Section 6 describes *in situ* treatment costs while Section 7 presents the conclusions and recommendations, based upon the results from the batch equilibrium tests and column tests. Section 8 presents the relevant references. The references are somewhat dated, as the most current reference cited was in 1986. Similarly, several of the figures, originally from photographs, were of very poor quality in the book, providing little, if any, information.

Appendices A and B present the data from the batch screening tests and the long-term stability column

tests, respectively. The dynamic flow leaching experiments were performed at pH 4.2 while the long-term stability column experiments were performed at pH 5.3. None of these leaching experiments were apparently performed in accordance with the EP-toxicity or TCLP protocols. It is unfortunate that the experiments were not performed using these well-accepted procedures.

The metal(s) mobility was considerably reduced with these immobilization techniques. The book presents much useful information relating to the immobilization of heavy metals in contaminated soils. To further minimize the potential for leaching after invoking immobilization techniques, capping the soils would prove helpful.

This book contains a wealth of information relating to the immobilization of heavy metals in contaminated soils. This book would be a good reference text for consulting engineers, plant managers, environmental managers, environmental public interest groups, and people involved in environmental restoration/site clean-up activities.

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Wastewater Treatment, by Paul N. Cheremisinoff, Pudvan Publishing Co., Inc., Northbrook, IL 60062, 1987, 348 Pages, U.S. List Price: \$24.95

The largest quantity of waste generated in households or in industry is typically wastewater. It is generated owing to the wide use of water for its tremendous power to clean, dissolve, and cool; and its low cost makes it the chemical of choice. Wastewater discharge from Publicly Owned Treatment Works and industries has taken on a new meaning with the current emphasis to minimize and/or eliminate the pollutants so as to protect human health,

aquatic life, and the environment. The wastewater discharge quality criteria is governed by the Categorical Wastewater Pretreatment Standards and the National Pollutant Discharge Elimination System Permits issued by the state agencies.

Traditionally, wastewater quality was monitored in terms of conventional pollutants, i.e., suspended solids, biological oxygen demand, pH, oil and grease, bacteria, and turbidity. With the advent of modern technology and its beneficial effects, the side effect is the generation and control of non-conventional pollutants, involving a gamut of organic and inorganic compounds in the wastewaters.

This book on wastewater treatment first presents the general treatment considerations of well established technologies to treat conventional pollutants. This is followed by a discussion of the methods for removing suspended solids using various filtration techniques and equipment. The author then deals with the methodology and equipment for removal of oily materials, phosphorus, and nitrogen from wastewaters. Conventional biological treatment processes are then discussed. The book concludes with a chapter on the removal methods for non-conventional organics and inorganics.

The intent of the book is to serve as a pocket handbook. Thus, it provides only the key information for the various unit operations and unit processes. The entire book primarily deals with conventional pollutants. Very little information is provided on the treatment for removal of non-conventional organic and inorganic compounds, which is of critical concern today in industrial wastewater management.

This book would be of value for those pollution professionals requiring a quick reference on the removal of conventional pollutants from wastewaters and for students in pollution or environmental engineering.

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Granular Activated Carbon: Design, Operation, and Cost, by Robert M. Clark and Benjamin W. Lykins, Jr., Lewis Publishers, Inc., Chelsea, MI, (1989). 342 pages [ISBN NO.: 0-87371-114-9] U.S. List Price: \$55.00

Activated carbon adsorption has been commonly employed in water and wastewater treatment operations for removal of trace level organic contaminants. This book summarizes design, cost, and performance information for application of granular activated carbon (GAC) in drinking water systems. The book emphasizes field-scale experience both in the United States and overseas. Both authors have considerable experience in the field and work in the Drinking Water Research Division, Risk Reduction Engineering Research Laboratory, with the U.S. Environmental Protection Agency (EPA).

The book contains eleven chapters. Chapter 1 provides a brief description of drinking water contamination and GAC treatment, including a discussion of the Safe

Drinking Water Act and its subsequent amendments.

Chapter 2 reviews GAC process design considerations, addressing such topics as carbon selection, contact time and breakthrough, breakthrough characteristics, breakthrough and system design, and design parameters (including adsorber characteristics, adsorber types and configurations, hydraulic loading, and backwashing). Also addressed in this chapter are reactivation systems, and carbon storage and transfer.

A number of EPA's field-scale studies are summarized in Chapter 3, while Chapter 4 deals with a comparative analysis of field-scale projects. Chapter 5 presents performance data of the virgin GAC systems. Chapters 6 and 7 discuss various types of reactivation systems and their performance, respectively.

Chapter 8 goes into the microbiology of GAC filtration and biological activated carbon, while Chapter 9 summarizes a number of models which have been used to describe the adsorption phenomena. Chapter 10 addresses control of trihalomethanes and synthetic organics

in terms of total organic carbon (TOC) removal, total organic halogen (TOX) removal, and total trihalomethane (TTHM) removal. Finally, Chapter 11 presents cost analysis information for granular activated carbon adsorption systems.

The references appear to be current and relevant. The primary criticism this reviewer has with the text is that the research work of Drs. C. P. Huang and Walter J. Weber, Jr. are not highlighted and emphasized more. Also, there is no discussion on the use of activated carbon adsorption for removal of heavy metals from solution.

In summary, the book is a good compilation of information on GAC adsorption systems. This book would be a valuable reference source for consultants, water utility managers, environmental engineers, university researchers, and water supply personnel.

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The Use of TK Solver for Environmental Engineering Problems

Ashok Kumar

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We need to solve problems involving equations (algebraic as well as differential) while working as environmental scientists/engineers in industry, regulatory bodies or universities. Solving such problems is a time-consuming task. It involves writing a computer program, debugging the program and then making required runs. Advances in personal computer software development in recent years will make our life easy in the near future. One such help is available to readers from Universal Technical Systems Inc., 1220 Rock Street, Rockford, IL. [Phone (815)/963-2220]. The company has developed TK SOLVER PLUS to meet our needs in solving problems. The software is a helpful tool to respond to "what-if" type of questions during decision making processes.

The software can be run on IBM PC/XT/AT/PS2, IBM AIX/RT, MACINTOSH, DECVAX, SUN and HP systems. The IBM PC version requires DOS 2.0 and 512 K RAM. The cost of IBM and Macintosh versions is \$395. Quantity discounts are available. A demo disk Mini TK is available for \$20. Use of a hard drive and a floppy drive is better than two floppy drives for using the program. The software can be run on a monochrome or color monitor. A help file is available.

The reference manual [1] is divided into five chapters. Syntax and semantics are discussed Chapter 1. The mechanism for performing arithmetic operations is described under "The Direct Solver" (Chapter 2). An overview of the Iterative Solver is given in Chapter 3. Built-in functions are explained in Chapter 4. The details of TK library are given in Chapter 5. Error messages given by the package are listed in Appendix A.

The introduction manual [2] consists of tutorial basic commands, sheets, list, rule functions, procedure functions, logical computations and complex variables. A chapter has been devoted to each topic. Three appendices are included in the book.

TK solves the problems using the Direct and Iterative Solvers. For Iterative Solver you are required to assign guess values to one or more unknown variables.

First of all I watched the slide presentations given on disk VIEW to get a feel for the software. Some examples on the disk are on curve fitting, roots of polynomials, matrix inversion, double integrals and TK graphics. Then I took a test drive on Mini TK. After reading seven pages of instructions on "How to Use Mini TK," I wrote a program for a jet plume model for short stacks [3]. I was able to compute ground level concentration as a function of downwind distance for a set of stack conditions. It was interesting to watch the computer acting like a calculator when I tried to find ground level concentration at different boundary points of the plant. The results can be obtained in tables and unit conversion can be automated.

The graphics is not included in Mini TK. Therefore, a college edition of the program [4] was tried. After reading the instructions in the manual, it was easy to obtain the graph of concentration versus downwind distance on the screen. I was not able to print the graphs in CGA mode. However, there was no problem in obtaining a copy of the graph on a personal computer with EGA configuration.

It is possible to interface with other programs. The files can be saved in DIF, WKS or ASCII formats. The full program comes with three floppy disks containing library models of math and statistic tools. It will take me some time to utilize the full potential of these models in my research.

A reference card comes with the packet which makes it easy to determine the various commands. It will take some time to get used to the TK commands. A TK/CAD link is also available which may be useful in designing pollution control equipment. Good support is provided by the company for the program and training courses are available for corporate clients.

One feature of the package which stands out during its use is the time saved in programming a model. My efficiency has increased significantly for solving day to day problems using TK. However, the solution of complex problems requires some learning of procedure functions.

Overall, I enjoyed using the program. I recommend its use to environmental professionals for solving mathematical problems and for training purposes.

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Pollution Prevention/Waste Minimization

Pollution prevention/waste minimization can be achieved in numerous ways. Reuse, recycle, reclamation, source control through good work procedures and housekeeping practices, and process changes are approaches for reducing wastes once they are formed. However, the best possible approach for pollution prevention/waste minimization is *waste elimination* through process modification, product change, or raw material change. The following describes how raw material substitution can reduce the volume of hazardous waste generated and reduce its toxicity. This improvement in waste management not only reduced the company's long-term environmental liabilities, achieved with a payback period for capital of less than one year, but is saving the company \$95,000 per year in operating costs.

R. Lee Byers
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Minimization section

Trivalent Chromium Electroplating Systems Offer Cost Savings as Well as Environmental Protection

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Much has been written in recent years about replacing environmentally hazardous hexavalent chromium electroplating solutions with trivalent ones for decorative plating applications. Although hexavalent processes have been used for electroplating for over 65 years, they have serious environmental and performance problems associated with them. Hexavalent chromium is a highly toxic material and a suspected carcinogen. Its use poses a danger to human health, particularly to shop personnel, as well as to the environment. Hexavalent chromium can escape the plating line through spills, leaks, in rinses and discarded baths, and in hydrogen bubbles formed during plating operations.

The performance deficiencies associated with hexavalent chromium use have been known for many years, but until recently attempts at developing alternative systems have met with only limited success. Recurring problems that result in reject parts and cost a shop owner money include:

- Poor covering power (especially around holes and slots)
- Burning
- White-washing
- Sensitivity to ripples in power supply
- Low energy efficiency. 90% of the electric power applied goes for the generation of hydrogen.

Large volumes of hazardous sludge are generated during reduction and neutralization of the wastewaters from hexavalent chromium processes. Hazardous waste haulage and disposal costs are rising dramatically each year. Thus it's becoming harder to use hexavalent systems profitably.

Advantages Offered by Trivalent Chromium Systems

Trivalent systems suitable for decorative chrome plating applications can reduce an electroplating shop's expenses in a number of ways:

1. **Lower Metal Concentrations.** Chromium concentrations in trivalent plating baths are typically less than 1 ounce per gallon (oz/gal). Hexavalent chromium concentrations range from 15 to 40 oz/gal. Lower heavy metal concentrations mean less waste treatment costs and less hazardous sludge generated in trivalent systems. Reducing sludge quantities also saves money in haulage and disposal fees.
2. **No Reduction Step.** By installing a trivalent system, the need to reduce hexavalent chrome wastes to their trivalent state can be avoided. Since three pounds of sodium metabisulfite are required to reduce each pound of chromic acid, significant quantities of chemicals, as well as equipment and labor costs, are eliminated by switching to a trivalent system.
3. **Rack Populations Can Be Increased.** Trivalent chromium chemicals produce a high quality plate even when rack densities are increased 15% to 25% above those for hexavalent chrome systems.
4. **Fewer Rejects.** The throwing power of trivalent chromium is excellent. It is difficult to burn parts, too, even with current densities above 100 amp/sq. ft. Trivalent systems do not experience the white washing problems that hexavalent systems do.
5. **Reduced Dragout.** Trivalent chromium baths are less viscous than hexavalent ones. Less solution clings to the parts that are withdrawn from the bath. This reduces both treatment expenses and material costs for the makeup chemicals.
6. **No Mist.** The eye-stinging, throat-irritating mist that is emitted from a chromic acid bath is almost completely absent in a trivalent system. The hexavalent chromium entrained in that mist is a suspected carcinogen. Besides being unpleasant to breathe, fumes from a hexavalent system present a danger to personnel and to the environment surrounding the shop.
7. **Reduced Liability.** Use of hexavalent chromium constitutes a liability to the shop due to the dangerous nature of the chemical. Spills and other accidental releases of hazardous wastes can lead to lawsuits that might have been avoided if safer chemicals were used.

Barriers to Trivalent Chromium Use

While trivalent chromium systems offer some distinct advantages over hexavalent chromium, there are potential problems associated with their use. In the past, color was a big problem. The plate was darker and not as shiny. This problem has been greatly reduced. The trivalent system developed by Canning Materials produces plates that are as shiny and of as high a quality as hexavalent chromium plates. If the trivalent chromium parts are placed side by side with hexavalent chromium parts, however, there is a noticeable color difference. This can be a problem in mixed batches of parts that have been plated using the two different methods. An example occurred in one Los Angeles shop that produced trivalent chromium wrenches sold in packages that also contain hexavalent chromium tools from another shop. Because of the color difference, the first shop was forced to use a hexavalent system to plate the parts.

The cost of chemicals for a trivalent system is currently higher than for a hexavalent setup, although this might change as trivalent systems become more common. Trivalent chromium systems are new, but have already demonstrated tremendous potential for the future. As waste management costs continue to rise, the savings that trivalent systems offer will increase markedly.

A Trivalent Chromium/Waste Minimization Success Story

Valley Plating is a medium sized chrome, nickel and zinc automated plating shop in the Los Angeles area. The shop converted an automated chrome line to a trivalent system two and a half years ago at a cost of \$70,000. It did this not for environmental reasons, but purely to increase profits. The owners felt that the increased production rate that they could achieve with a trivalent system would outweigh the higher costs of plating chemicals. They were right.

The shop found that at least 15% more surface area of parts could be placed on each rack in the new trivalent system without a drop in quality, increasing production from 1050 ft² to 1200 ft² per hour. And the reject rate, which was one in every 65 parts in the hexavalent system, is now less than one in 200 parts. Because trivalent waste streams don't require a reduction step or generate as much sludge as hexavalent systems, treatment chemical requirements and waste disposal costs have been dramatically reduced.

Trivalent plating chemicals cost the shop over \$100 more per shift than the old chemicals, but this cost has been more than offset by the trivalent system's advantages. The increase in profits for Valley Plating's new trivalent line amount to \$180 for each 8-hour shift. Since the shop runs two shifts a day, annual profits have been increased by \$95,000. The capital cost for the trivalent system was more than offset within the first year.

Trivalent systems have not been developed that can reliably meet the specifications for hard chrome plating, but they appear to offer a viable, profitable alternative to hexavalent systems for decorative chrome applications.

November 11-16, 1990. AIChE's 1990 Annual Meeting will be held at the Palmer House, Chicago, Illinois. Meeting Program Chair: Charles Wentz, Argonne National Laboratory, 9700 S Cass Avenue, ES/362, Argonne, IL 60439 (708/972-7693). Committee Meeting Coordinator: Yvonne Armstrong, AIChE (212/705-7344). For registration information, contact AIChE Meetings Department, 345 E. 47th St, New York, NY 10017 (212/705-7320).

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Removal of Volatile Organic Compounds from Water and Wastewater—William Byers, CH2M Hill, POB 428, Corvallis, OR 97339-0428 (503/752-4271), Fax (503/752-0276) & Bill Cobb, CH2M Hill, 2020 SW 4th Ave, 2nd Fl, Portland, OR 97201-4953 (503/224-9190).

Area 9c: Solids-Coordinator: David Kosson, Chem and Biochem Eng Dept, Rutgers Univ, Piscataway, NJ 08854 (201/932-4346).

Preliminary Assessment of Federally Owned Nuclear Processing Facilities—Dale Keairns, Westinghouse Electric Corp, 1310 Beulah Rd, Pittsburgh, PA 15235 (412/256-1954) Fax (412/256-1348) & Jim Thiesing CH2M Hill, 6121 Indian School Rd NE, Suite 122, Albuquerque, NM 87110-4140 (505/884-5600) Fax (505/883-7507).

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Area 9d: Process Development—Coordinator: Jacoby Scher, Pilko & Assoc, Inc, 2707 N Loop W, Suite 960, Houston, TX 77008 (713/861-1417) Fax (713/861-6210).

Process Design for Waste Reduction—Jacoby Scher (see above) & Larry Southwick, VP, 23272 Mill Creek

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Industrial Practices of Processing Recycled Plastics—Donald White, Dept of ChE, College of Eng & Mines, Univ of AZ, Tucson, AZ 85721 (602/621-6044) Fax (602/621-4189) & Wayne Pearson, Plastics Recycling Foundation, Inc, POB 189, Kennitt Sq, PA 19348 (215/444-0659) Fax (215/444-4744).

R&D Progress on Processing Recycled Plastics—Donald White (see above) & Nick Schott, Dept of Plastics Eng, Univ of Lowell, North Campus, Ball Hall, 1 Univ Ave, Rm 204, Lowell, MA 01854 Fax (508/452-1445).

Area 9e: Legislation and Regulation-Coordinator: Richard Siegel, ENSR, 35 Nagog Park, Acton, MA 01720 (508/635-9500) Fax (508/635-9180).

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Fundamental Chemical and Physical Processes in the Atmosphere (Cosponsored by Group 9a)—John Seinfeld, ChE Dept, Cal Tech, Pasadena, CA 91125 (818/356-4635) Fax (818/795-1547) & Viney Pal Aneja, Dept of Marine Earth & Atmospheric Sci, NC State Univ, Raleigh, NC 27695 (919/737-7808) Fax (919/737-7802).

Use of Genetic Engineering in Pollution Control—Robert Irvine (219/239-6306) & Michael Gray (219/239-5380), Dept of Civil Eng, Univ of Notre Dame, Notre Dame, IN 46556 Fax (219/239-8007).

Fundamentals and Applications of Adsorption Processes—Robert Peters (see above) & Dibakar Bhattacharyya (see above).

Waste Solidification/Stabilization Fundamentals, Treatment Technologies, and Applications—Marty Tittlebaum, Civil Eng Dept, LA State Univ, Baton Rouge, LA 70803 (504/388-8508) Fax (504/388-5990).

The Impact of Internal Phosphorus Loading on the Restoration of Trout Lake

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The accelerated eutrophication of many lakes by society is a problem of increasing concern. The increase in photosynthetic productivity may decrease water clarity, alter dissolved oxygen profiles, and decrease the aesthetic value of a lake. For those lakes which possess high levels of water quality, the need for lake management arises. The first step in developing management techniques for any lake is to collect baseline data—primarily measurements of temperature, dissolved oxygen, transparency, and calculation of a lake's morphometric parameters. Beaulac, Reckhow, and Simpson (1980) [1] indicate that the analysis of lake water nutrient concentration (phosphorus/nitrogen) and calculation of annual nutrient budgets are important additions to baseline data. By studying a lake and its watershed, relationships fundamental to the development of lake prediction models may be determined which operate as a function of nutrient-related parameters such as the areal phosphorus and water loading to a lake. Quantitative changes in phosphorus loading can be interpreted to provide changes in lake water phosphorus concentration and subsequently trophic status. Predictions made through the use of such models serve as a basis for management decisions.

INTRODUCTION

Limnologists and other resource scientists have become concerned with methods of removing pollutants and preventing excess nutrient loading to lakes. Trout Lake, located in Itasca County near Coleraine, Minnesota, provides a case in point as it has experienced a reduction in water quality over the last 40 years. This decline was induced by the flow of nutrient-laden effluents from the Bovey-Coleraine sewage treatment plant. As a result of this decline in water quality the first step in the restoration process—sewage diversion—took place in 1987. Since the recovery of a lake after sewage diversion may be delayed by internal phosphorus loading (e.g. Shagawa Lake, Minnesota, Larsen *et al.*, 1981 [2]) it is important to consider the impact of this problem for Trout Lake. Because the resource is an important asset of the Coleraine community, a study which compiles baseline data, assesses the current trophic status, and composes a list of possible alternatives for restoring previous water quality standards to Trout Lake was highly desirable.

During the past two years, a limnological evaluation was carried out on Jessie Lake in Itasca County involving measurement of current trophic status, a phosphorus budget, and development of a phosphorus model to be used for future management of the lake. Based on this background, it was found desirable to continue work in this field by applying this technology to a new lake management problem—the sewage treatment plant diversion

and restoration of Trout Lake. Since this lake is only 25 miles from Jessie Lake, information regarding export coefficients and modeling principles was useful for the Trout Lake study.

OBJECTIVES

Essentially there were three objectives to the study on Trout Lake during 1987. The primary objective of this study was to develop a working prediction model for Trout Lake based on Vollenweider's (1975) [3] concept that could be used to predict total lake phosphorus concentration after phosphorus abatement. It was found necessary to investigate the degree of anoxic conditions as well as phosphorus concentrations in Trout Lake's hypolimnion to determine the presence of internal phosphorus loading, and subsequently develop a correction factor for the model to account for this loading. As part of this objective, an attempt was made to determine the lake's internal phosphorus release rate through laboratory experiments by making comparisons with actual lake measurements. Such a test would be valuable for future monitoring of the internal release rate.

The second objective of this study was to obtain baseline data for Trout Lake including measurements of dissolved oxygen, temperature, and pH. This also included calculation of some of the lake's morphometric characteristics. The third objective of the study was to determine the current trophic status of Trout Lake using the procedures outlined by Carlson (1977) [4]. This included the measurement of Secchi disk transparency, chlorophyll *a*

J.S. Goetzman was co-winner of the AIChE Environmental Division Student Paper Contest 1989.

concentration, and total phosphorus concentration of the lake. The total phosphorus index value was to be given precedence for the indication of trophic state, as this nutrient is the factor limiting algal production and was also analyzed in more detail with respect to the number of samples taken, adding to the reliability of the expressed value.

METHODS

From April to October of 1987, Trout Lake was monitored semimonthly for dissolved oxygen, temperature, chlorophyll *a*, and total phosphorus. Trout Creek, the lake's outlet, was also sampled to determine water flow and total phosphorus concentration. Weed samples were taken in August to investigate the potential of harvesting lake plants as a means of lake trophic state restoration.

Three sampling stations were chosen for the 1987 study. These stations were located on the north, center (deepest portion), and south regions of the lake. In addition to the three lake stations, a single station was chosen along the outlet for monitoring water flow and total phosphorus concentration leaving the lake.

Dissolved oxygen and temperature readings were obtained using a dissolved oxygen meter. Profiles of both temperature and oxygen were taken from 1 to 30 meters on each sampling visit. Oxygen profiles were an important aspect of baseline data, as the depth and time period for which the lake remained anoxic was information needed for determining internal phosphorus loading.

Secchi disk readings were determined using a standard black and white plastic Secchi disk with the actual transparency found as the mean of the depths at which the disk disappeared and reappeared. Chlorophyll *a* and total phosphorus concentrations were determined through colorimetry using a Beckman Model 20 spectrophotometer. The procedure used for analysis of total phosphorus concentration was the persulfate digestion method. These values were used with Carlson's Index (1977) [4] to determine trophic status.

In August 1987, samples of cattails, lily pads, and bullrushes were taken as these represent the major population of plants in the littoral zone of Trout Lake. Population was determined by counting the number of individuals within a frame constructed of four meter sticks. Samples consisted of 10 plants in the square meter which were later dried, weighed, and analyzed for phosphorus content.

In addition to determining internal phosphorus release rates by measurements in Trout Lake, an attempt was made to determine phosphorus release rates by recreating oxic and anoxic conditions in the laboratory. Anoxia was created by adding 5 grams of corn starch to 1 liter of water of known phosphorus concentration in a vacuum

bottle and evacuating the bottle. Thus, the anoxic condition was created by a combination of the high biological oxygen demand (BOD) of the corn starch and the loss of oxygen due to evacuation of the bottle. Oxic conditions were created by aerating 1 liter of water, also of known phosphorus concentration, using a simple aquarium pump. Each bottle was then supplemented with 10 or 30 grams of Trout Lake sediment from a filter cake made by combining 4 bottom samples obtained from different areas of the lake at spring turnover using an Ekman dredge. All bottles were left for a 6-week period with 5-ml samples being drawn off at designated time intervals for total phosphorus and dissolved oxygen measurements.

RESULTS AND DISCUSSION

A number of morphometric parameters were calculated for Trout Lake. The first parameter, mean depth (\bar{Z}), calculated as the volume of the lake divided by its surface area, was determined to be 15.2 meters. Mean depth is often regarded as the best single index of morphometric conditions and usually shows a general inverse correlation to productivity at all trophic levels among large lakes. However, a deep lake such as Trout Lake that has become eutrophic by human influence over a few years varies from this relationship and thus, offers an opportunity to be restored to oligotrophic status.

Trout Lake's dissolved oxygen content was monitored from April to October 1987 to determine when and at what depth the lake turned anaerobic (anaerobic indicates values less than 1.0 mg/l dissolved oxygen), since oxygen depletion leads to increased phosphorus loading from the sediments. Trout Lake became anaerobic in mid-July as shown by the oxygen profiles in Table 1.

Approximately 30 total phosphorus samples were analyzed from Trout Lake's epilimnion, giving a range of 0.022 to 0.078 mg/l with a mean summer concentration of 0.050 mg/l. Carlson's Trophic State Index (TSI) [4] is based upon parameters including total phosphorus; thus, the values obtained in the study were also used to determine the trophic status of Trout Lake. Based upon lake total phosphorus concentration alone, Trout Lake would be ranked as an eutrophic lake, with a TSI value of 60. This is according to the following relationship between Carlson's TSI and traditional trophic characteristics: ultra-oligotrophic, <27; oligo-mesotrophic, 27-37; meso-eutrophic, 37-53; eu-polytrophic, 53-71, polytrophic, >71.

Chlorophyll *a* is often associated with algae and consequently with lake water studies. Chlorophyll *a* is the second parameter which was monitored in 1987 to use in classifying Trout Lake. Chlorophyll *a* analyses on Trout Lake ranged from 0.4 to 16.7 $\mu\text{g/l}$ with an average concentration of 5.4 $\mu\text{g/l}$ which would rank Trout Lake as a meso-eutrophic lake with an index value of 47.

TABLE 1. SUMMARY OF DISSOLVED OXYGEN (MG/L) AND TEMPERATURE (°C) MEASUREMENTS FOR TROUT LAKE—SUMMER 1987

Depth, m	June 23		July 15		July 24		August 27		September 9	
	Temp.	Oxygen	Temp.	Oxygen	Temp.	Oxygen	Temp.	Oxygen	Temp.	Oxygen
1	26.0	7.9	22.0	10.0	24.5	10.9	21.0	8.6	19.0	9.5
4	21.2	6.1	21.0	9.4	24.0	10.7	20.0	8.4	18.5	9.4
6	18.5	5.8	21.0	9.4	21.3	7.7	20.0	8.1	18.5	9.1
8	14.8	4.8	19.0	8.0	20.0	6.7	20.0	7.9	18.5	8.9
10	12.2	4.4	13.5	4.6	15.8	4.1	19.5	7.4	18.0	8.1
13	11.5	4.0	11.5	4.0	12.3	2.5	12.5	0.6	13.5	0.8
15	10.5	3.8	11.0	3.6	11.0	2.2	11.8	0.5	11.5	0.8
18	10.0	3.6	10.5	3.3	10.3	1.3	11.0	0.4	11.0	0.7
21	9.5	3.3	10.0	2.6	10.0	0.7	10.5	0.5	10.5	0.7
25	9.5	2.9	9.5	2.4	9.8	0.8	10.0	0.5	10.0	0.7
27	9.0	2.6	9.5	2.4	9.5	0.6	10.0	0.5	10.0	0.5
29	9.0	2.5	9.5	1.9	9.5	0.8	9.5	0.4	10.0	0.4

TABLE 2. SUMMARY OF MEAN VALUES FOR TOTAL PHOSPHORUS, CHLOROPHYLL *a*, AND SECCHI DISK WITH CALCULATED TROPHIC INDICES

1987 Date	Total Phosphorus (mg/l)	Secchi Disk (m)	Chlorophyll <i>a</i> (µg/l)	Trophic State Indices		
				Secchi Disk	Chlorophyll <i>a</i>	Total Phosphorus
April 26	0.072	2.1	6.8	49	50	66
May 2	0.047	4.6	0.5	38	22	60
June 23	0.050	1.6	16.1	54	69	61
June 29	0.038	2.4	—	48	—	57
July 7	0.115	2.6	—	46	—	70
July 15	0.039	3.2	3.4	43	42	58
July 24	0.037	2.6	—	47	—	57
July 30	0.025	3.0	—	44	—	51
August 13	0.037	2.2	3.5	48	43	57
August 27	0.036	2.8	—	45	—	56
September 9	0.032	3.0	—	44	—	55
September 23	0.046	2.7	—	46	—	60
October 8	0.058	—	—	—	—	63

Secchi disk transparency was measured from April through October during which time 25 readings were obtained ranging from 1.4 to 4.8 meters. Based on Secchi disk alone, with an average value of 2.7 meters, Carlson's Index at 46 would rank Trout Lake as meso-eutrophic. It should be noted that Secchi disk and chlorophyll *a* measurements were made in deep areas of the lake where rafts of algae could be avoided. This probably leads to higher uncertainty in these values thus accounting for the lack of correlation between the index values of both Secchi disk and chlorophyll *a* versus that of total phosphorus. A summary of the measurements and TSI values is given in Table 2.

The development of more specific management techniques requires both morphological and hydrological data regarding the lake in question. These data include information as to phosphorus loading, mean depth, lake flushing rate, and residence time. These can be used with the basic equation ($P = L/q_s(1 - R_{pred})$), to predict phosphorus concentrations if the required parameters can be determined for the lake being studied. This model works well for lakes with oxalic hypolimnia, as was documented by Goetzman (1987) [5]. The investigator followed recent developments in lake phosphorus modeling by estimating Trout Lake's annual water and phosphorus budgets. This method relies upon the use of phosphorus export coefficients, precipitation loading coefficients, and calculation of watershed size.

Water may flow into lakes from many sources including direct precipitation, creeks or inlets, and springs. An estimate of the volume of water entering a lake annually may be obtained by multiplying the watershed area by the depth of runoff. For Trout Lake it was also necessary to add the volume of effluents flowing to the lake annually from the Bovey-Coleraine sewage treatment plant. The volume of water entering Trout Lake annually was determined to be 6.61×10^6 m³. Based on this estimation of inflow, a calculation of areal water loading, flushing rate, and mean residence time was made. Before sewage diversion, areal water loading (which describes the entering volume of water as a loading per unit of lake surface area) was calculated to be 0.86 m/yr. The flushing rate was found to be 0.057 lake volumes per year, while mean residence time was found to be 17.5 years.

TABLE 3. EXAMPLES OF TOTAL PHOSPHORUS CONCENTRATION (MG/L) PROFILES

Depth, m	June 29	July 30	August 27	September 23
1	0.038	0.025	0.036	0.046
10	0.094	0.064	0.031	0.098
20	0.100	0.118	0.260	0.280
30	0.160	0.198	0.470	0.420

Total mass flow of phosphorus to a lake is best estimated by summing the annual contributions from each of the nonpoint sources plus additional point sources within the watershed. For Trout Lake this included the inputs from runoff, precipitation, urban runoff, homes or cabins, and the treatment plant. Each of these inputs was calculated, giving a mass loading of 2749 kg/yr which is equivalent to 0.359 g/m²/yr. With this external phosphorus loading value, a retention coefficient of 0.921, and the water loading of 0.86 m/yr, the predicted spring phosphorus concentration using the model previously discussed was 0.033 mg/l. This is considerably lower than the measured value of 0.075 mg/l.

Thus, it was a primary objective of this study to modify the oxalic model to include internal phosphorus loading in Trout Lake to provide a more accurate prediction of the lake's actual phosphorus concentration. The release of phosphorus from the sediments is often affected by the amount of oxygen available, as insoluble complex ferric iron compounds are reduced to soluble ferrous iron compounds. This allows for the release of phosphorus back into the water. Thus, oxygen concentrations were used in conjunction with phosphorus profiles (Table 3) and calculation of water volumes by planimetry to calculate the internal phosphorus loading to Trout Lake in 1987.

The first step in determining internal loading was to calculate phosphorus concentrations in Trout Lake for two portions based on the oxalic/anoxic boundary (as determined by oxygen sampling) for each sampling date (Figure 1). The volume of water in each portion was then calculated and a phosphorus concentration from the current profile was multiplied by the volume of water under each condition (oxic or anoxic) to determine the mass of phosphorus in the lake. By subtracting the minimum value of the spring from the maximum value in the fall, a phosphorus loading of 4417 kg was found for the period between turnovers. Since a percentage of that loading was due to external sources, an appropriate amount was subtracted leaving an internal loading of 4153 kg. This was equivalent to a loading value of 0.542 g/m²/yr, which was incorporated into the new prediction model for Trout Lake.

Because sewage diversion took place in 1987, the water and phosphorus budgets for the lake for future years will be altered. After diversion, the annual volume of water inflow was found to be 6.06×10^6 m³ and the new areal water loading was 0.79 m/yr. The flushing rate of Trout Lake was determined to be 0.052 per year, while the new residence time was found to be 19.1 years. Since the total amount of phosphorus entering the lake has been reduced by the sewage diversion, a new annual mass loading was found to be 827 kg/yr—a 70% reduction. When this value was used in the new model with the internal

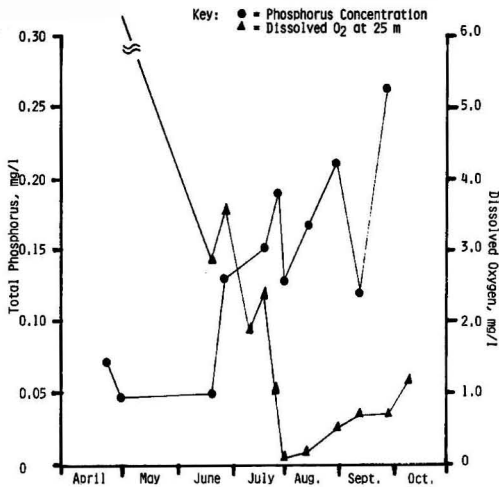


Figure 1. Variability of total phosphorus concentration in the anoxic portion of Trout Lake with respect to dissolved oxygen at 25 meters in depth. Summer 1987.

loading figure ($0.542 \text{ g/m}^2/\text{yr}$), a new spring turnover concentration of 0.061 mg/l was predicted for Trout Lake. Since changes from one steady state to another are exponential, Garn and Parrott (1977) [6] suggest that the time required to complete the change can be estimated using a half-life calculation. As a result of this calculation for Trout Lake, it is predicted that it will take 5–10 years to reach the 0.061 mg/l concentration from the current 0.075 mg/l .

To develop a method of assessing changes in the internal phosphorus release rate, a series of bottle tests were carried out with benthic mud taken at spring turnover. A test period of six weeks was used with bottles containing 1 liter of lake water of known phosphorus concentration and an anoxic condition. Samples were taken from the bottles each week for the analysis of phosphorus. Results for tests using 10 or 30 g of sediments showed similar rate curves with about 30% and 10% of the phosphorus present going into solution, respectively. The increase in phosphorus concentration was fairly rapid during the first

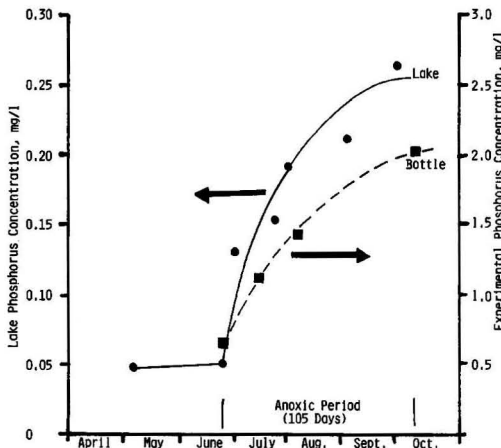


Figure 2. Change in phosphorus concentration of the anoxic portion of Trout Lake during summer 1987 compared with experimental values.

three weeks and then seemed to slow up to a fairly constant rate. Release rates were correlated to that which was observed in Trout Lake during the sample period in 1987 to provide a means of comparison for future years as shown in Figure 2.

The result of this study indicates that Trout Lake could be slow to recover without some means to reduce the internal phosphorus load from sediments under the persistent anoxic hypolimnia. Thus, as part of the study, information on several restoration alternatives was obtained. For example, tests run to look at the effect of alum in retarding phosphorus release indicated that sediment and water conditions in Trout Lake may be amenable to this kind of treatment if costs were reasonable. A second method considered was harvesting of biomass which was investigated by sampling and analyzing various lake weeds. Data from these tests showed 0.3 to 10.4 g/m^2 of phosphorus could be removed by harvesting the areas of heavy weed growth. However, cost and disruption of the lake would have to be considered. The effect of other restoration techniques such as flushing or oxidation can also be calculated with the lake model developed.

CONCLUSIONS

Several conclusions may be drawn as a result of the 1987 study on Trout Lake. First, based upon total phosphorus concentrations, the lake could be considered eutrophic with a TSI value of 60. Second, the Trout Lake model, $(P) = (L_{\text{ext}} + L_{\text{int}})/13.7 q_s$, can be used to predict and assess future impacts on the lake's trophic state due to restoration procedures. This was shown by assessing the impact of sewage diversion, as the Trout Lake model predicts a spring turnover concentration of 0.061 mg/l for the lake after sewage diversion. When compared with the 0.075 mg/l turnover concentration measured in 1987, this shows some improvement in Trout Lake's water quality, but the lake remains eutrophic. However, this concentration will not be attained for 5–10 years, as estimated by a half-life calculation based on the lake's flushing rate. Third, an experimental procedure was developed to determine internal phosphorus release rates using a novel approach to creating anoxia in the laboratory. Results of these tests were correlated to lake release rates to provide a method to monitor lake release rates without heavy field sampling. Alternative restoration methods such as using alum or weed harvesting were shown to be effective and should be studied further with consideration of the economic and social impacts.

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Technical, Economic, and Regulatory Evaluation of Tray Dryer Solvent Emission Control Alternatives

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Public awareness and government agency attention have focused on emissions of organic compounds as a principal cause of the increased levels of ozone and smog in the ambient air across the nation. Evaporation of solvents from tray dryers, used in many applications in the chemical, pharmaceutical, and surface coating industries, potentially contributes significantly to the problem. Selecting and designing control equipment to comply with toughening solvent emission regulations is complicated by the needs to dilute the solvent concentration (for safety reasons) and by the emission profile which shows high initial emission rates declining over the drying cycle. There is no single control technology that will automatically satisfy all regulatory, economic and technical requirements. This article presents a comparison of several common control technologies applied to tray dryer solvent emissions based upon technical and economic considerations.

INTRODUCTION AND EMISSIONS ASSESSMENT

The mixing of solid crystal multi-components into a uniform blend is a process required in the formation of many chemical and pharmaceutical products. However, such large-scale blending is inexact, time-consuming, and energy-intensive and can add considerable expense to manufacturing operations.

Propeller-driven mixing of solid components, suspended in a liquid medium, is more efficient and uses less energy. To be useful, however, the liquid medium must not react with or otherwise alter the solid components being blended. Water and other inexpensive organic solvents, such as isopropanol, toluene, and naphtha, are most commonly used in industry as the liquid carrier. There are many solids which are incompatible with water, necessitating the use of solvents or a combination of the two.

After blending is completed, the granulation must be dried by evaporating solvent from the suspension. Typically, the solvent-laden solids are placed onto trays which are loaded onto racks and wheeled into room-sized ovens. The wet granulation is dried, commonly at temperatures from 60°C to 82°C (140°F to 180°F) for long periods of time (often 8 to 48 hours). This is particularly true

in the pharmaceutical industry, where FDA standards preclude the presence of any solvent in the final product. Figure 1 shows the solvent evaporation rate during a typical drying cycle in a small unit.

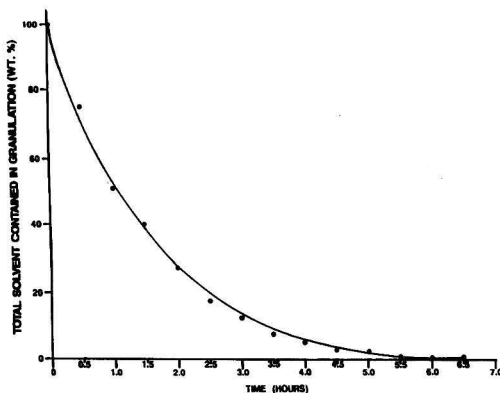


Figure 1. Solvent content of wet granulation during typical drying process.

Tray drying operations result in a significant amount of solvent emissions. After being drip dried, the wet solid granulation typically contains about 1 kilogram (kg) of solvent for every 6 kg of wet solids (although this ratio is variable). A typical industrial oven may be loaded with 500 kg of wet solids per batch and emit the total organic solvent content of about 80–100 kg into the atmosphere.

The solvent emission rate is not constant throughout the drying cycle. Rather, the solvent content of the wet granulation decreases in a nearly exponential fashion dependent upon solvent volatility, oven operating temperature and air exhaust rate, with approximately 40% to 50% of the total solvent in the granulation generally emitted during the cycle's first hour. Figure 2 shows the volatile organic compound (VOC) emission profile of a recently-tested drying oven, loaded with about 430 kg of wet solids, containing 64 kg of isopropanol (IPA). This represents a small to medium size industrial operation. VOC emissions were determined by differential weighing every half hour of 12.5% of the total trays used. Results from an actual run are shown. A second run showed a very similar profile.

REGULATORY ASPECTS

Regulations controlling VOC emissions have grown more complex in the 1980s because many areas of the country are not in attainment with ambient ozone concentration standards (most VOCs undergo photochemical reactions in the atmosphere to form ozone and other components of smog). Enforcement of such regulations has been and will be further tightened by many federal, state, and local agencies because many regions of the country have remained non-attainment past federally established deadlines and because of the imminent reauthorization of the Clean Air Act (expected in 1990).

Nearly every state and many local districts have regulations applicable to general VOC emissions, although they vary in specificity. For instance, at least 20 states have regulations specific to the pharmaceutical industry, many written with batch-type emissions (such as those from tray dryer operations) in mind.

The most common regulation requires total emissions of VOCs from batch drying to be limited to 33 lbs (15 kg) per day, unless potential emissions exceed 330 lbs (150 kg) per day, in which case 90% control of the potential daily emissions is required. At least 20 states have regulations that are identical or similar to this (AL, AZ, CA, CO, CT, DE, GA, IN, KY, LA, MD, MI, MO, NC, NY, OH, PA, TN, TX, WI).

A smaller number of locales limit VOC emissions on an hourly basis or on both an hourly and daily basis. If the

hourly emission rate limit is exceeded, a specified control efficiency (ranging from 75% to 95%) must be applied. Such regulations are enforced in DC, NJ, PR and VA.

In addition to regulations aimed at curbing VOC emissions from sources in general or from specific industries, many states have further restrictions on VOC emissions based upon pollutant toxicity. These regulations limit emissions on the basis of stack concentration and are based on factors such as the toxicity of the pollutant, stack height, stack exit velocity, distance to receptors, and worst case maximum emission rates. These impact heavily on drying processes because of the high initial emission rate and the potential health effects of solvents such as toluene, isopropanol and naphtha.

VOC EMISSION CONTROL OPTIONS

A number of viable options have been developed to control organic solvent emissions. While several control technologies may not be feasible for most tray dryer applications, all the major technologies are reviewed to assure that all options are considered.

Condensation

Organic vapors may be condensed, in practice, by extracting heat. Surface condensers are designed to allow an optimal surface area for vapor cooling and collection of the condensate.

Most condensers are of the shell and tube type, in which coolant flows on the shell side, lowering the temperature and thereby condensing the organic vapors flowing inside the tubes. The fraction of the vapors which condense inside the tubes can then be collected.

The degree of control of organic vapors in a condenser is proportional to the vapor pressure of the pollutant, with greater control achieved as the temperature drops. Thus, the coolant used dictates the operating temperature in the condenser and the percentage of organic vapor collected. Coolants commonly used include water (which lowers the hot vapor temperature to 15°C to 27°C, or 60°F to 80°F), chilled water (final temperature of 2°C to 7°C, or 35°F to 45°F) and chilled glycol, brine or refrigerant (final temperature of -62°C to -7°C, or -80°F to +20°F).

Gas Absorption

The gas absorption process controls emissions by promoting the contact of organic vapor with a liquid medium capable of absorbing it. The control efficiency is dependent upon the surface area exposed, residence time, solubility of the vapor in the liquid, and the degree of chemical reaction. Gas absorption equipment is designed to provide thorough contact between the media in order to permit interphase diffusion of these materials.

Some common absorbers include packed towers, impingement plate towers, and venturi absorbers, all of which increase gas/liquid contact by dispersing the liquid in the vapor-laden vessel. Equipment is available to disperse the gas stream in the liquid.

Packed towers disperse the liquid medium by means of inert solid packing material, providing the longest residence time of any gas absorber type and making them the preferred option for vapors which have low solubilities. Mass transfer is maximized in countercurrent tower operation.

Another common gas absorber type is impingement plate towers. Plates in the tower disperse the vapor into many small gas bubbles, increasing the vapor interfacial area and thus allowing greater absorption by the liquid.

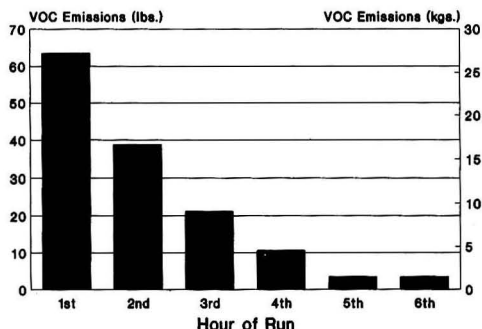


Figure 2. VOC emissions from an actual drying oven (hour by hour basis).

This is the preferred method when low liquid rates are required or for dilute pollutant concentrations.

Venturi scrubbers optimize contact between vapor and liquid by introducing the gas stream into the liquid at high velocity. The liquid is then atomized into small droplets which, by baffling, disperse throughout the free space of the chamber, maximizing liquid contact with the vapor. The high speeds of the vapor stream reduce residence time while increasing the contact surface area. Venturi scrubbers are more often used to control fine particulates, but have been used in some applications to control organic vapors.

Carbon Adsorption

In the carbon adsorption process, organic molecules adsorb onto activated carbon. Activated carbon is an excellent medium for organic adsorption based upon carbon's affinity for organic molecules and the large surface area for adsorption. The organics may be desorbed and recovered, and the carbon reused.

Most systems are designed to pass the organic-laden air stream downward through a fixed granular carbon bed. Flowing carbon or the use of powdered carbon can lead to entrainment in the exhaust. In dual bed units, the type most commonly used, one carbon bed is in operation adsorbing organic vapors while the other is regenerated (commonly with steam) to remove adsorbed organics. If the organics removed are soluble in water, then an aqueous solution is obtained for disposal. If they are insoluble or slightly soluble, an oily organic phase can be recovered for disposal. The aqueous phase may contain some organic residue and must be properly disposed of. This usually involves obtaining new wastewater discharge permits.

Carbon adsorption is most useful when the organic concentration of the air stream is high and recovered compounds can be reused. Carbon adsorption systems must be well designed and monitored to minimize and detect contaminant breakthrough.

Incineration

Another major approach to organic vapor control is incineration, the high temperature oxidation of hydrocarbons to carbon dioxide and water. The two major types of incineration are thermal and catalytic.

Thermal oxidizers or afterburners are devices which expose the solvent-laden stream to temperatures above the solvent's autoignition point for a sufficient time for complete oxidation to occur. Generally, the combustion temperature is maintained at a minimum of 650°C or 1200°F (and an average of about 816°C or 1500°F) and residence time from 0.5–1.0 second to obtain a destruction efficiency of 90% to 99%. Another factor affecting destruction efficiency is adequate mixing of the solvent stream in the chamber.

Although the oxidation of organics releases heat, auxiliary fuel burning may be needed to maintain the required temperatures if solvent concentrations are insufficient. Heat recovery is usually employed because the temperature of the incinerator flue gas is high, and the waste heat may be used to continuously preheat incoming the solvent-laden stream or to supply heat to the drying oven.

Catalytic oxidizers control organic emissions by the same oxidation reactions, but are conducted on a catalyst bed (generally made of platinum or palladium). A major advantage of catalysis is that it requires a much lower temperature for oxidation than thermal systems, thereby reducing supplemental fuel requirements. Catalytic incinerators usually operate at 315°C–427°C (600°F–800°F),

with a residence time normally of 0.3–0.5 second, resulting in a reduction of supplemental fuel requirements. However, for catalysis to be effective, the stream must be free of substances that can cover or clog the effective surface area, such as particulate matter. Also, the problems of disposal of spent catalyst and the high cost of replacement of catalyst units must be considered.

TRAY DRYER VOC EMISSION CONTROL REQUIREMENTS

Before the technical and economic feasibility of each technology can be assessed, the VOC control requirements of the particular tray dryer must be understood. Differences in such factors as quantity of wet solids loaded, percent volatile organic, solvent quantity and composition, and individual regulatory requirements need to be considered. Some general guidelines are presented.

As discussed earlier, VOCs are emitted at a much greater rate during the initial hours of the drying cycle compared to the latter stages. As a result, design and planning of VOC control equipment must take into consideration the large VOC inputs in the early part of the cycle and relatively small loads toward the middle and end of the cycle.

The regulations pertaining to many applications of the oven drying of solvent-laden granulation mandate a control efficiency of VOC emissions of the entire batch, as well as maintaining records of wet solids input into the oven. This allows consistent operating conditions of the control device if a satisfactory control efficiency is guaranteed. For those applications where emissions are limited by an hourly rate, operating conditions may need to be altered for compliance, while resources are not misused.

TECHNICAL AND ECONOMIC FEASIBILITY

This section presents an analysis of the feasibility of several control technologies, and discusses the technical and economic parameters needed to achieve compliance with general regulations. These technologies include condensation, absorption, carbon adsorption, and incineration. For those technologies deemed feasible, an economic evaluation will be presented.

A simplified example provides a basis for comparison of technology types: a single drying oven which dries a number of products. The "worst case" batch contains 180 kg of IPA which must be evaporated. The oven is operated at 65°C, and it is assumed that during the initial (peak) hour of operation, 90 kg of IPA is emitted, approximating a small to medium sized industrial drying oven; 90% control of the IPA in the batch must be achieved.

The first design criterion for the oven is the determination of the exhaust air flow rate. A high flow rate results in an air stream dilute in IPA, thus increasing the capital and operating costs of the control device. A low flow rate, however, may result in IPA concentration build-up in the oven approaching its Lower Explosive Limit (LEL). Generally, the solvent concentration should not exceed one-quarter of the LEL. Since the LEL of IPA is 2%, or 20,000 ppm, one-quarter of the LEL is 0.5%. Peak IPA emissions of 90 kg/hr are equivalent 36.0 sm³/h (21.5 scfm derived below) which, when divided by 0.005, results in an exhaust rate of 7300 sm³/h (4300 scfm). At 65°C (150°F), this is equivalent to 8500 m³/h (5000 acfm). For added safety, an exhaust rate of 10,200 m³/h (6000 acfm) is used. Variable air flow controls are available, which allow the flow rate to be lowered as the solvent concentration in the oven exhaust air declines.

Condensation

Condensers are effective in reducing emissions of vapor streams with high solvent concentrations. The organic concentration at the condenser outlet is determined by the vapor pressures of the organics at the temperature in the condenser. If the contaminant in the air stream is pure, the condensate may be recovered and reused. Achieving 90% control of a typical solvent-laden exhaust in the early part of the heating cycle requires a large degree of vapor pressure reduction. Brine or ethylene glycol, kept at subfreezing temperatures, may be required for most industrial solvent tray dryer applications.

To obtain 90% control of the IPA of the entire batch, the condenser must be designed for at least 90% control during the worst case peak hour. With an input to the condenser during the first hour of operation of 90 kg of IPA:

$$\frac{90 \text{ kg}}{\text{hr}} \times \frac{1000 \text{ gm}}{\text{kg}} \times \frac{1 \text{ gm-mole}}{60.1 \text{ gm}} \times 0.024 \frac{\text{sm}^3}{\text{gm-mole}} = 36.0 \text{ sm}^3/\text{h of IPA}$$

The standard volumetric flow rate of the system at this point is equivalent to:

$$10,200 \text{ m}^3/\text{h} \times \frac{20^\circ\text{C} + 273}{65^\circ\text{C} + 273} = 8840 \text{ m}^3/\text{h}$$

The mole fraction of IPA entering the condenser is:

$$\frac{36.0}{8840} = 0.004$$

Using a design requirement of 90% control of the peak hour emission rate, the mole fraction of IPA must be reduced to 0.0004. This is equivalent to a saturation vapor pressure of:

$$0.0004 \times 760 \text{ mm Hg} = 0.31 \text{ mm Hg}$$

To reach this saturation vapor pressure, a temperature of about -40°C must be maintained in the condenser. Consequently, the energy expenditure required to maintain this temperature precludes the use of condensation as a viable alternative.

Condensers are not recommended for most industrial tray drying applications because of the very low temperatures needed to condense 90% or more of the organic vapor in the stream, the resultant high energy cost required to maintain these temperatures, the potential of

water freezing in the condenser, and the problems of disposal of the condensate if it cannot be reused. However, a surface condenser using cooling water may be useful upstream of other control devices, particularly if the oven exit temperature is not optimal for the operation of the main control device.

Absorption

A packed tower with a once-through water system can effectively reduce emissions of water soluble organics such as IPA to meet regulatory requirements. Wet scrubbers can readily reduce IPA emissions by greater than 90% at loads of 90 kg/hr or more.

One disadvantage of wet scrubbing an IPA-laden stream is the cost of disposing the IPA-laden water. Modifications to existing wastewater discharge permits may be required.

Based on the example provided in this section, wet scrubbing is a candidate as a control device because isopropanol is highly soluble in water. To achieve 90% or greater control of IPA during peak load, a packed tower with 3 meters of packing can be operated to optimize IPA-water contact. Generally, 2.5 cubic meters of water or more is required for every thousand cubic meters of exhaust gas to achieve greater than 90% control. Water usage would total approximately 0.4 cubic meters per minute in this example under peak conditions.

The installed capital cost of such a packed tower, including blower, exhaust ductwork, stack, interconnecting piping and valves, and controls is approximately \$90,000, based upon a purchase price of \$50,000. Annualized costs, including depreciation, interest, taxes, utilities, insurance, and maintenance total approximately \$55,000, and are outlined in Table 1.

Scrubbers do not effectively remove water insoluble organics, such as toluene. Although scrubbing may be attempted with a non-volatile organic, such as mineral oil, the process is inefficient and expensive, particularly at low solvent concentrations. Mineral oil would need to be reused to be cost effective; however, desorption of absorbed solvent is prohibitively expensive. Therefore, wet scrubbing of a solvent such as toluene is not a feasible alternative.

Carbon Adsorption

Activated carbon can effectively reduce solvent emissions from tray dryers if the system is properly designed and maintained. Problems that may hinder adsorption of solvent include the presence of particulates, water or water solvent azeotropes in the inlet stream. In the oven, granulation should be covered to minimize particulate

TABLE 1. ECONOMIC COMPARISON OF EMISSION CONTROL ALTERNATIVES (6,000 ACFM OR 10,200 M³/HR SYSTEM)

Alternative	Total Installed Cost (1,000)	Annualized Capital Cost (\$1,000)	Annual Operating Cost (\$1,000)	Total Annualized Cost (\$1,000)
Packed Tower (Once Through Water)	90	27	28	55
Carbon Adsorption w/Solvent Recovery	275	83	45	128
Thermal Incineration w/50% Heat Recovery	300	90	100	190
Catalytic Incineration w/50% Heat Recovery	350	105	60	165

Notes:

1. Cost presented in December 1989 dollars.
2. Annualized capital cost is 30% of total installed cost which includes: depreciation at 10%; interest at 11%; taxes, insurance, and administrative charges at 4%; and maintenance and labor at 5%.
3. Annual operating costs based on 4,000 hr/yr of operation, electricity at \$0.10/kwh, natural gas at \$0.60/therm, water at \$1/1,000 gals (\$4.72/1000 m³), carbon at \$3/lb (\$1.36/kg), steam at \$8/1,000 lbs (\$1.76/100 kg) and labor at \$20/hr.

entrainment and the resulting fouling of the activated carbon, and reasonable action should be taken to reduce the inlet stream humidity. Lowering of the inlet temperature is advantageous because the carbon adsorption process is exothermic.

Removal of IPA using activated carbon is not cost-effective because IPA has a low adsorptive capacity, and large systems would be required to remove the necessary amounts of IPA from typical industrial tray oven applications. As previously discussed, IPA can be easily and economically removed by wet scrubbing.

Toluene can be more efficiently controlled by carbon adsorption than IPA due to the organic nature of the activated carbon. Using the example provided in this section with toluene as the pollutant rather than IPA, carbon adsorption is a candidate as a control device because of toluene's affinity to carbon. A dual bed system is suggested, allowing regeneration of one unit during operation of the other. If an oven has a large enough down-time, then a single bed may be used.

Based on an adsorption efficiency of 7 kg of toluene per 100 kg of carbon and a requirement of 90% control of the 180 kg of toluene in the batch:

$$\frac{162 \text{ kg toluene controlled}}{\text{batch}} \times \frac{100 \text{ kg carbon}}{7 \text{ kg toluene}} = \frac{2314 \text{ kg carbon}}{\text{batch}}$$

Use a 3000 kg carbon per bed.

The bed should be regenerated shortly after the drying cycle because of the high temperatures in the system. Steam may be used to remove toluene from the bed. At a rate of about 10 kg of steam per kg of adsorbate, at least 1633 kg of steam are required for one cycle. Although the toluene and water form different phases, the water phase may contain up to 500 ppm toluene and must be disposed of properly.

The capital cost of an installed dual bed carbon adsorption system for a single oven to remove the required amounts of toluene (3000 kg carbon per bed) is approximately \$275,000, based upon a purchase price of \$200,000 and an installation cost of \$75,000. Annualized costs, taking into consideration the capital costs, utilities, cooling water, carbon replacement, recovered solvent, depreciation, taxes, insurance, and maintenance, total approximately \$128,000. A breakdown of these costs is outlined in Table 1.

Thermal Incineration

The main advantage of thermal incineration compared to other control technologies is its ability to reduce emissions of low concentration solvent streams. Control effi-

ciencies of over 99% have been achieved for well designed and maintained afterburner units.

The size of an incineration unit is directly dependent upon the volumetric flow of the inlet stream to be combusted and the required residence time. For the example given, the design volume of 2.83 m³ is obtained, based upon 10,200 m³/hr and 1.0 sec. average residence time.

The energy costs required to operate a thermal incineration unit are estimated from the heat load required to raise and maintain the air stream temperature to the combustion temperature in the incinerator, assuming negligible solvent heating value. Thermal incineration is energy-intensive, because auxiliary fuel is generally required to maintain the proper combustion temperature. Heat recovery, in the form of preheating the inlet stream or heating the drying oven itself, can reduce this energy cost.

In terms of regulatory compliance, thermal incineration offers the user the major advantage of high control efficiencies. With theoretical control efficiencies of over 99%, afterburners will not become obsolete when regulations are changed to require greater control efficiency.

Catalytic Incineration

Catalytic incineration, like the thermal type, can result in control efficiencies of over 99%. However, the specific advantages of catalytic systems over thermal units include reduced auxiliary fuel requirements, smaller size units, and the elimination of the need for high temperature materials of construction.

In terms of economics, the normal operating temperature range of the process (600°F–800°F or 315°C–427°C) allows some heat recovery. Offsetting this, the cost of catalyst and the possibility of catalyst fouling by impurities in the waste stream add to operating costs. Annualized capital and operating costs of thermal and catalytic incinerators are presented in Table 1.

In summary, incineration is very cost-ineffective for combustion of large volumes of air with low heat content, i.e., air with a low concentration of combustible solvents. Drying ovens tend to operate at a highly aerated state to prevent the combustible concentration from approaching the LEL. Thus, unless a facility operates a number of very large ovens, incineration is not an economical method to control solvent emissions from tray dryers.

CONTROL STRATEGIES

By combining our understanding of the emission profile of the drying operation, the characteristics of the solvent and the regulatory requirements, a suitable control system can be designed and operated to minimize costs and resource utilization, while meeting regulatory requirements.

Most of the solvent emissions occur in the first few hours of the drying cycle, and only very dilute VOC streams are exhausted during the last few hours. For dry-

TABLE 2. COMPARISON OF VOC EMISSION FROM AN ACTUAL DRYING OVEN USING DIFFERENT CONTROL STRATEGIES

Hour	Uncontrolled VOC Emissions (kg)	Controlled (90%) VOC Emissions (kg)	VOC Emissions (kg) Using Initial Overcontrol Strategy
1st	28.80	2.88	1.44
2nd	17.60	1.76	0.88
3rd	9.62	0.96	0.48
4th	4.81	0.48	0.24
5th	1.59	0.16	1.59
6th	1.59	0.16	1.59
7th-Termination	0	0	0
Totals (kg)	64.01	6.40	6.22

TABLE 3. ASSESSMENT OF FEASIBILITIES OF CONTROL TECHNOLOGIES FOR TRAY DRYER PROCESSES

Technology	IPA Control	Toluene Control
Condensation	Technically Infeasible	Technically Infeasible
Gas Adsorption (Wet Scrubbing)	Feasible	Technically Infeasible
Carbon Adsorption	Economically Infeasible	Feasible
Thermal Incineration	Economically Infeasible	Economically Infeasible
Catalytic Incineration	Economically Infeasible	Economically Infeasible

ing operations in which the solvent emissions are limited on a total batch basis, the control system can be designed and operated to achieve a greater removal efficiency during the initial hours of operation, and then shut down or bypassed during the latter hours, thereby minimizing operating costs while still achieving environmental goals.

In the actual example given in Figure 2, 90% control of the tray dryer batch solvent emissions may be achieved after 4 hours of operation at 95% control because emissions predominate during the early part of the cycle. Table 2 compares VOC emissions of the drying oven using 90% control throughout the entire cycle versus using 95% control during the first 4 hours only. Bypassing the control equipment for the remaining hours of the cycle will result in savings of resources and energy, while still attaining the mandated 90% control of the entire batch's emissions.

For drying processes using IPA-water mixtures, the wet scrubber may need to be operated for a longer period because the presence of a less volatile component (water) dampens the sharpness of the IPA emission curve.

SUMMARY

Based upon technical and economic considerations of the various control technologies, ratings such as feasible, technically infeasible, and economically infeasible have been given. Table 3 provides a summary of this comparison. Overall, for a simple tray drying system, wet scrubbing is the preferred system for controlling emissions of water-soluble VOCs, while carbon adsorption is the preferred system for controlling water-insoluble VOCs. A thermal or catalytic incinerator is preferred for more complex systems where input may vary greatly, both quantitatively and qualitatively. Some situations that may warrant incineration include large operations involving several ovens or other VOC-emitting sources emitting varying amounts of different contaminants simultaneously. The selection of the appropriate control technology depends upon regulatory emission requirements, site-specific utilities and space constraints, capital and operating costs, waste disposal requirements, and system reliability and maintenance requirements.

EPA's Assessment of European Contaminated Soil Treatment Techniques

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Site remediation is a pressing issue in European countries due to limited availability of land. Therefore, much progress is being made in the development of effective technologies for remediating contaminated sites. The purpose of the program described in this paper was to investigate the most successful and innovative European technologies for potential introduction into U.S. markets. Phase I of this EPA-sponsored project was a 9-month research effort which identified 95 innovative technologies in use or being researched in foreign countries. During Phase II, the most promising technologies identified in Phase I were studied in-depth through personal interviews with the engineers who research and apply these technologies, and through tours of laboratory models and full-scale installations. Phase III of the assessment effort culminated in the first forum on innovative domestic and international hazardous waste treatment technologies on June 19-21, 1989, in Atlanta, Georgia. The most successful full-scale technologies investigated were developed in the Netherlands and West Germany. These technologies include vacuum extraction of hydrocarbons from soil, in situ washing of cadmium-polluted soil, in situ steam stripping, and a number of landfarming and soil washing operations. The paper provides description of 11 soil remediation techniques that have shown such promise in laboratory studies or in practice to warrant consideration of their use in the United States, and summary information on the international technologies selected for presentation at the Phase III forum as they relate to soils remediation.

BACKGROUND

The following paper summarizes the results of a 9-month study by the U.S. Environmental Protection Agency's (EPA) Office of Program Management and Technology.

The purpose of this EPA program was to identify and assess international technologies applicable to hazardous waste site remediation in order to promote their use in the United States. As shown in Figure 1, the program was conducted in three phases: 1) Phase I: Technology Iden-

tification and Selection; 2) Phase II: Technology Review; and 3) Phase III: Forum on Innovative Domestic and International Hazardous Waste Treatment Technologies. This paper focuses on the results of Phase II and Phase III of the program.

GENERAL APPROACH

The Phase II investigation of the most promising technologies was accomplished by interviewing scientists and engineers who are researching or have extensive experience with each technology. Meetings at laboratories, facilities, and site installations were scheduled by Alliance Technologies Corporation or organized by the coordinators of treatment technology research in each country. Key coordinators from foreign countries include Ms. Esther Soczó, Coordinator of Soil Development at The National Institute of Public Health and Environmental Hygiene (RIVM), the major government research center in the Netherlands; and Mr. Christian Nels, Director of Research for Umweltbundesamt, the Federal Republic of Germany's equivalent of the U.S. EPA. During the Phase II investigation, 13 technologies in three European countries were visited by the field team [1].

Phase III of the project, the *Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and In-*

ternational, was attended by over 530 representatives from the U.S. and 7 other countries. Scientists and engineers representing U.S. and international government agencies, industry, and academia attended 30 presentations and 40 poster sessions describing successful case studies of physical, chemical, biological, thermal, and stabilization treatment methods.

OVERVIEW OF SITE REMEDIATION PROGRAMS IN THE NETHERLANDS, BELGIUM, AND FEDERAL REPUBLIC OF GERMANY

Although the Phase I efforts reviewed site remediation technologies from all parts of the world outside the U.S., the Phase II investigation focused on technologies in the Netherlands, Belgium, and the Federal Republic of Germany. Other countries such as France, Italy, and Denmark are also involved in extensive technology development. However, much of the work in those countries is already being documented by the NATO/CCMS Pilot Study Demonstration program [2]. The Phase I Technology Identification and Selection Report [3] summarizes the status of site remediation programs and technology development in many countries.

A brief overview of the site remediation programs in the Netherlands, Belgium, and Federal Republic of Germany follows below.

The Netherlands

The field team began its Phase II efforts in the Netherlands, a very densely populated country where landfilling of wastes is highly restricted. Remediation of abandoned hazardous waste sites has become a priority in the Netherlands. Extensive experience with land and water management has expedited the development of soil and water management techniques useful for site remediation.

The Dutch government has three sets of soil concentration levels for hazardous contaminants which are used as guidelines for prioritizing site remediation. Table 1 shows the three reference levels designated "A," "B," and "C." Soils with contamination above the "C" level, if treatable at a cost below 250 Dfl/tonne (\$135/ton), must be cleaned to below the "B" level concentrations. Soil contaminated below the "B" level, but above the "A" level, may be used as fill in road or building construction. Soils cleaned to concentrations below the "A" level may be left in place.

The Dutch government supports the development of innovative site remediation techniques through the research center, TNO (Netherlands Organization for Applied Scientific Research), and by partially funding cleanup efforts. The Dutch government also provides full support of the research and development center, RIVM (National Institute of Public Health and Environmental

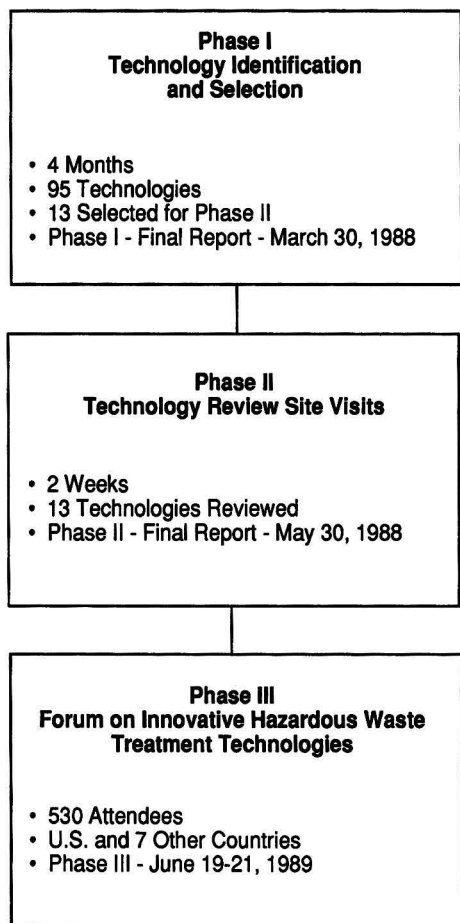


Figure 1. Program structure.

TABLE 1. DUTCH REFERENCE LEVELS USED FOR THE JUDGEMENT OF SOIL CONTAMINATION

Component	Concentration level (mg/kg dry weight)		
	A	B	C
Polycyclic aromatic hydrocarbons (total)	1	20	200
Mononuclear aromatics (total)	0.1	7	70
Mineral oil	100	1,000	5,000
Cyanide (total complex)	5	50	500

A = Background level uncontaminated soil.

B = Level which necessitates further investigation.

C = Level which necessitates a sanitation investigation.

Hygiene). Representatives from the Dutch government and industry are active in the NATO/CCMS Pilot Study Demonstration Program.

Belgium

Although the three regions of Belgium are encouraging development of regional treatment facilities, little information was available concerning site remediation efforts. At this time, very little site remediation work is being conducted in Belgium due apparently to a lack of government spending and regulation in this area. However, a potentially useful high temperature technique for the treatment of low-level radioactive wastes was investigated for possible application to difficult-to-treat hazardous wastes.

The Federal Republic of Germany (West Germany and Berlin)

Unlike the Netherlands, the Federal Republic of Germany (FRG) has not yet set limits for the concentrations of contaminants in soil. Using the Dutch tri-level system as a guideline, the German state governments collaborate with responsible parties on reasonable goals for final concentrations on a site-by-site basis.

Treatment technology development is promoted by Umweltbundesamt, the West German equivalent of the U.S. EPA, through a 50 percent funding program. Technologies that qualify can receive a 50 percent loan on capital costs for pilot-plant construction. If the pilot project is successful, the technology must be employed and the loan must be repaid. If the plant fails to reach preset performance goals, the company does not have to repay the loan. West German site remediation experts are also active in the NATO/CCMS Pilot Study Demonstration Program.

One activity that has helped to stimulate site remediation in the Federal Republic of Germany was a mandatory insurance requirement beginning in the late 1960s for companies with oil and gasoline storage tanks. These policies have been broadened to include most hydrocarbon-contaminated sites and have encouraged development and application of inexpensive and effective oil treatment techniques.

SUMMARY OF PHASE II RESULTS

The field team visited 12 research groups, consultants, and manufacturers at 15 locations in three countries in Europe. The site visits, conducted from March 21 through April 2, 1988, during the Phase II effort, are listed below by country and researcher or manufacturer.

The Netherlands

1. TNO
 - Electrochemical treatment of organohalogenes
 - Bioreactors
2. RIVM
 - Overview of soil treatment research in the Netherlands
 - *In situ* bioremediation
3. Heijmans Milieutechniek BV
 - Soil washing by extraction
4. TAUW Infra Consult BV
 - *In situ* washing of cadmium-polluted soil
 - Rotating biological contactors for treatment of pesticides in ground water
5. HWZ Bodemsanering
 - Soil washer for cyanides

6. Heidemij Uitvoering BV

- Mobile soil washer using froth flotation
- Steam stripping *in situ*
- Cum-Bac onsite composting technique

Belgium

1. SCK/CEN
 - High Temperature Slagging Incinerator

Federal Republic of Germany

1. Hannover Umwelttechnik GmbH
 - Vacuum extraction of organics in soil
2. Umweltbundesamt
 - Overview of soil treatment research in the FRG
3. Harbauer GmbH
 - Soil washing using low frequency vibration
4. TBSG Industrievertretungen GmbH
 - Soil cleaning onsite using the surfactant "Oil CREP"
5. Umweltschutz Nord GmbH
 - Onsite composting using bioreactors, special substrate, and reed beds
 - *In situ* bioremediation

In general, the Phase II efforts were successful at identifying site cleanup technologies not currently used in the United States, as well as unique applications of techniques used in the United States. Among the most important Phase II findings related to soil remediation were five different soil washing techniques in the Netherlands and the FRG. In addition, the field team reviewed unique applications of *in situ* biological treatment and composting techniques, vacuum extraction, *in situ* air stripping, and *in situ* extraction of cadmium from soils. The results of the most important Phase II site visits related to soil remediation are summarized below.

Soil Washing Equipment Findings

The field team reviewed five high-throughput soil washing technologies in the Netherlands and the FRG. Characteristics of these technologies are summarized in Table 2, including throughput, unit operations, reject particle size, and costs.

A key similarity among all of the units is that they operate on the principle that most of the contaminants are sorted to the fine materials (<63 μm) and segregation of these materials from the other size fraction "cleans" the soil. Some of the units (*i.e.*, the Heijmans unit) employed very simple particle separation and wash water treatment technologies, while others (Harbauer and Oil CREP) employed more sophisticated extractants and cleaning agents. A major consideration of all washing techniques is the fact that as particle reject size decreases, so does sludge residue generation. Cleaning efficiency tends to decrease with decreasing particle reject size as well.

Although it is impractical to discuss the details of each soil washing technique in this article, a brief discussion of the HWZ soil washing operation in Amersfort, the Netherlands, will serve to illustrate a typical soil washing unit. The HWZ unit was approximately the median in size and complexity of unit operations among the soil washing units investigated. One atypical feature of this unit is that 30 percent of the wash water was discharged to a nearby estuary, whereas many of the other units employed 100 percent recycle of wash water.

The HWZ soil cleaning method is based on techniques of soil washing and particle sizing, along with a water

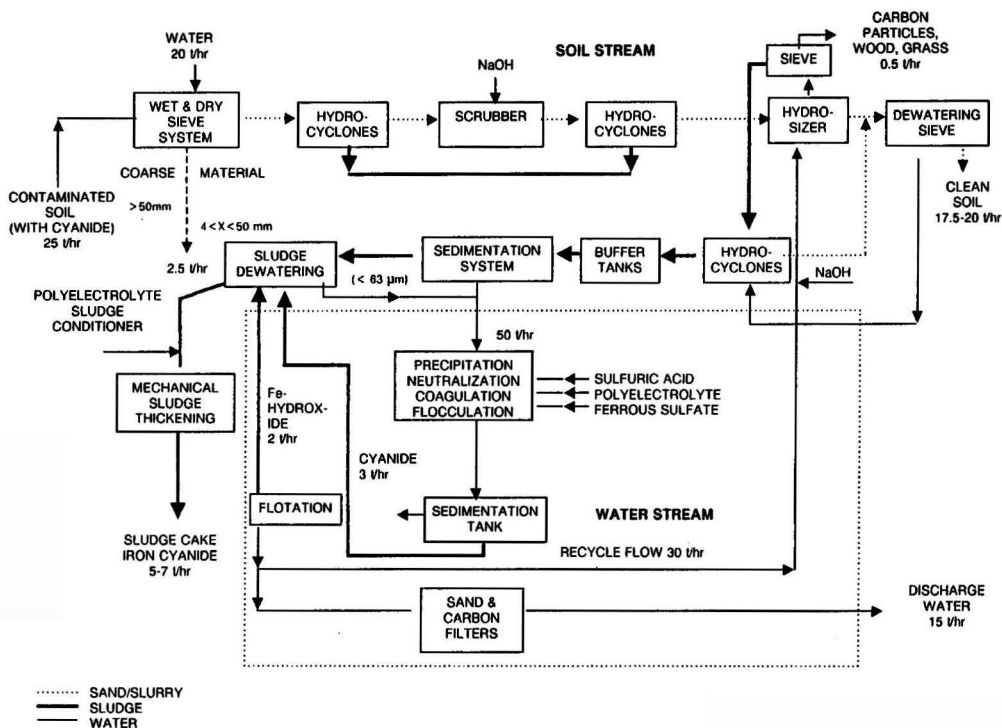
TABLE 2. SOIL WASHING INSTALLATIONS VISITED BY ALLIANCE/EPA FIELD TEAM IN MARCH 1988 IN THE NETHERLANDS AND THE FEDERAL REPUBLIC OF GERMANY

Installation	Rated throughput	Principal operations	Particle reject size	Fixed or transportable	Pollutants treated	Refractory pollutants	Treatment fee per ton	Sludge disposal costs per ton	Capital costs
Heijmens Milieutechniek b.v. Rosmalen, the Netherlands	11 tons/hr	Particle sizing Scrubbing with detergents and oxidants Flocculation Precipitation	<63 μm	Transportable but fixed	Cyanides Heavy metals PCAs Mineral oil Kerosene	Cl-HCs Aromatics	\$73-91 \$102 at max 30% <63 μm	\$136	New 33 tons/hr plant planned \$4.5 million
HWZ Bodemsanering Amersfoort, the Netherlands	22 tons/hr	Particle sizing Scrubbing with detergents Flocculation pH adjustment Carbon Filters	<63 μm	Transportable but fixed	Cyanides Heavy metals Aromatics Solvents Cl-HCs	Oily cmpds Br cmpds	\$53 plus \$2.50/ton for each % <63 μm , up to 20%	\$136	\$3 million
Heidemij Uitvoering b.v. 's-Hertogenbosch, the Netherlands	30 tons/hr	Particle sizing Froth flotation with cleaning agents Washing	<50 μm	Mobile, but will be fixed in the future	Cyanides Heavy metals PCAs Oils ClO HCs Pesticides	PANs PCBs HCH Some heavy metals	\$90-155, 2200 tons is min treated	as high as \$182	\$3 million
Narbauer GmbH Berlin, FRG	16.5-22 tons/hr	Particle sizing Low-freq. vibration with extractants Washing Water treatment by flotation, air stripping, ion exch. and activated carbon	<15 μm	Fixed	Organics Phenol PAH Org-Cl cmpds PCBs	Heavy metals	\$136 (excludes residue disposal)	Sludge stored at date	\$4.5-6 million
TBSC Industrievertretungen GmbH-Oil CREP System Bremen, FRG	44 gpm. New 88 gpm plant planned	Particle sizing Washing with Oil CREP I Solid/liquid separation	<100 μm	Mobile	Extractables HCs PAHs Extr. Hal-org.	PCBs Fl-HCs Cyanides Heavy metals	\$82-109 excluding disposal of residues, 3920 cu yds min treated	\$6K/day sludge treatment	Not known at this time

treatment stream. A flow schematic of the system is shown in Figure 2. After first crushing the larger pieces of rubble, pieces 4 mm < x < 50 mm are separated out of the stream by wet sieving. Soil particles 63 μm < x < 4 mm comprise the main soil stream. These particles are washed of adsorbed contaminants by scrubbing with detergents and adjusting the pH to 12-13 by addition of NaOH. The HWZ soil scrubber employs two mixing propellers, one mixing up and the other mixing down, with a net flow downward. A hydrosizer then removes low density organic and carbon particles such as wood and rubber. After a dewatering step, the remaining sand (63 μm < x < 4 mm) is often clean enough to be used in asphalt batching; if not, it must be landfilled. The fines (<63 μm) are separated by hydrocyclones and dewatered in a belt press. The remaining contaminants are

concentrated in this small volume of fines and disposed of as hazardous waste.

The contaminated scrub water and the overflow from the wet sieves, hydrocyclones, and belt press are cleaned in the water treatment stream. After residual fines are removed by sedimentation, the water is treated in a tank by precipitation, neutralization, coagulation, and flocculation to remove the dissolved contaminants. Cyanide can be removed here by the addition of ferrous sulfate. In the last steps of the water treatment stream, floating iron hydroxide particles are removed by sand filtration, and dissolved organics by activated carbon. The cleaned water is then discharged or recycled. The treatment of soil contaminated with bromine compounds has been successful on a laboratory-scale, but has not yet been tested on a full scale.



Adapted from: Breek, H.C.M., written correspondence to J. Hyman of Alliance, March 16, 1988. [1]

Figure 2. HWZ soil treatment scheme.

In general, pollutant levels and removal efficiencies achievable by soil washing strongly depend on the distribution of the pollutants over the different size fractions and the presence of soil particles other than sand (such as adsorbing clay and carbon particles) which are difficult to wash. The contaminants trapped in the clay clumps cannot be reached by scrubbing, but if the clumps are crushed, the contaminants can be taken out in the sludge. Where the amount of the fine fraction is greater than 20 percent, the volume reduction of the contaminated soil is generally not sufficient to warrant treatment.

Most of the soil washing companies noted that their practical upper limit of fines (<63 μm) was 20 to 30 percent in the soil to be cleaned. Because the proportion of fines present increases the generation of sludge, treatment costs tend to increase for finer grained soils. The Harbauer technology offers the advantage of potentially generating less sludge; however, the additional costs of wash water treatment employed for that technology make it slightly more expensive than the other soil washing technologies reviewed.

Heijmans, which is among the more simply designed systems, accepts soils with fine fractions up to 30 percent, but their process works best on sandy soils with a minimum of humus-like compounds. Because no sand or charcoal filters are employed by Heijmans, the system is not able to treat such contaminants as chlorinated hydrocarbons or aromatics. Like most soil washing techniques, the throughput and cost of treatment are dependent on the quantity of fine fractions in the soil to be cleaned.

The Heijmans system has had its greatest success treating soil contaminated by cyanides (CN). Heijmans adds hydrogen peroxide (H₂O₂) into the scrubber to react with CN to form CO₂ + NH₄. In one experiment, CN at a con-

centration of 5,000 to 6,000 mg/kg dry soil was reduced to 15 mg/kg. The results of the use of the Heijmans soil washer on seven different types of contaminated soil is shown in Table 3.

TABLE 3. RESULTS OF SOIL CLEANINGS PERFORMED BY HEIJMANS MILIEUTECHNIEK B.V. (ANALYSES PERFORMED BY AN INDEPENDENT LABORATORY)

Site	Soil type	Contaminant	Before (mg/kg)	After (mg/kg)
Galvanizing	Silt	Total cyanide	250-500	10-15
		Chromium	43-45	11-15
	Sand	Nickel	250-890	40-70
		Zinc	460-720	140-200
Fuel drilling	Coarse sand	Kerosene	5,000-7,000	80-120
Galvanizing	Fine sand	Total cyanide	400-1,000	6-10
		Chromium	100-2,500	70-120
		Cadmium	4-18	0.5-1.4
		Copper	100-250	25-60
		Nickel	100-600	50-80
		Lead	100-450	20-70
Gasworks	Fine sand	Total cyanide	80-220	5-15
	Coarse sand	Total PCAs	250-400	0.5-10
Diesel fuel	Silt	Mineral oil	3,000-8,000	90-120
	Fine sand			
Galvanizing	Coarse sand	Total cyanide	75-300	7-10
		Zinc	160-170	50-80

Translated from the brochure "Heijmans Milieutechniek b.v. Bodemsanering, Installatie Voor Het Reinigen Van Grond," January 1988 [4].

Vendor-supplied cleaning efficiency data for the other four soil washing units are summarized in Table 4 for a variety of contaminant types. In general, the efficiencies for heavy metals and cyanides are similar among the units. The Oil CREP unit tends to be more efficient for hydrocarbon wastes and the Harbauer unit has advantages in soils with higher clay content.

Other Unique Applications of Site Remediation Technologies

During the trip, many other successful applications of conventional and novel treatment technologies were observed, on both a research scale, as well as full-scale. Table 5 outlines the important characteristics of these technologies.

Bioremediation research and full-scale application of bioremediation technologies have advanced in European countries much as they have in the United States. During visits with two research organizations (TNO and RIVM) and three consulting companies, the field team observed many successful studies and applications of biological treatment technologies, mostly aerobic systems.

In situ bioremediation was researched and tested at RIVM and applied by Heidemij in the Netherlands. RIVM found that hydrogen peroxide was a suitable oxygen source for *in situ* bioremediation. Biodegradation rates of 10 mg C/kg/day were obtained by RIVM. At a contaminated gasoline site, bioremediation will be used for cleanup to the Dutch "A" limit of 20 mg/kg.

Onsite bioremediation technologies are being researched and applied in both the Netherlands and the FRG. TNO showed successful results from laboratory experiments for both wet slurry biological treatment systems and dry compost-type systems. This fundamental research showed diffusion of organics from the soil particles to be the rate limiting step. Full-scale applications of compost-type systems were being applied by both Heidemij (the Netherlands) and Umweltschutz Nord (FRG). Costs for full-scale *ex situ* composting applications were reported to be in the range of \$82 to \$136/ton.

Another physical/chemical treatment method reviewed included an *in situ* cadmium extraction project by TAUW. The cadmium extraction project employed *in situ* hydrochloric acid leaching of cadmium from over 30,000 m³ of soil. The acid leachate was purified by ion exchange and

reused. The treatment cost was estimated to be \$75/ton of soil.

Numerous full-scale projects involving *in situ* vacuum extraction and air stripping of volatile contamination were reviewed in the FRG. Hannover Umwelttechnik (HUT) has installed over 300 vacuum extraction systems for vadose zone decontamination. HUT has also developed a unique *in situ* air stripping system for removing volatiles from ground water in conjunction with vacuum extraction. Treatment costs for the HUT system are less than 10 DM/tonne (\$5/ton).

SUMMARY OF PHASE III RESULTS

The Environmental Protection Agency's Office of Program Management and Technology hosted a three day international conference in Atlanta, Georgia, to exchange solutions to hazardous waste treatment problems. Over 530 representatives from the U.S. and 7 other countries attended the *Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International* on June 19-21, 1989. During the first-ever meeting of its kind, scientists and engineers representing U.S. and international government agencies, industry, and academia attended 30 presentations describing successful case studies of physical, chemical, biological, thermal, and stabilization treatment methods. In addition to the many presentations, domestic and international scientists and vendors prepared over 40 posters.

Many of the presentations specifically addressed soil remediation. Speakers from West Germany and the Netherlands gave six presentations on physical/chemical treatment methods including soil washing, froth flotation, vapor extraction, and infiltration. Four biological treatment methods in use in West Germany were discussed. Four presentations on thermal treatment of soils were given by speakers from the Netherlands, Switzerland, and West Germany. In addition, participants in EPA's Superfund Innovative Technology Evaluation Program described their projects.

One of the presentations at the forum that generated excitement was a description of "electroreclamation" of heavy metals and other contaminants from soil and ground water. The method, refined by the Dutch firm, Geokinetics, is based on the migration and collection of

TABLE 4. SUMMARY OF SOIL WASHING PERFORMANCE FOR OTHER SYSTEMS

Pollutant	Harbauer GmbH ^a			Heldemij Ultravopring ^b			HWZ Bodemsanering ^c			Oil CREP System ^d		
	Input	Output	Removal efficiency (%)	Input	Output	Removal efficiency (%)	Input	Output	Removal efficiency (%)	Input	Output	Removal efficiency (%)
Total organic (mg/kg)	5,403	201	96.3	—	—	—	—	—	—	—	—	—
Total phenol (mg/kg)	115	7	93.9	—	—	—	—	—	—	—	—	—
PAH (mg/kg)	728.4	97.5	86.6	19	0.34	98.2	100-150	15-20	86.0	1,131	46.5	95.9
Extractable org-Cl compounds (mg Cl-/kg)	90.3	n.d.	100	5.3	0.4	92.5	—	—	—	—	—	—
PCB (mg/kg)	3.2	0.5	84.1	—	—	—	—	—	—	7.2	0.30	95.8
Cyanide (mg/kg)	—	—	—	200-1,000	5	99.2	100-200	5-15	93.3	—	—	—
Pesticides (mg/kg)	—	—	—	650	14.4	97.8	—	—	—	—	—	—
Oils, hydrocarbons (mg/kg)	—	—	—	>1,000	65	93.5	—	—	—	1,785	22.3	98.8
Oil, toluene, benzene (mg/kg)	—	—	—	3,000-18,000	20	99.8	—	—	—	—	—	—
Chlorinated hydrocarbons	—	—	—	276	0.5	99.8	20-30	>1	96.0	—	—	—
Heavy metals (mg/kg)	—	—	—	—	—	—	300	75-125	66.7	—	—	—
Pb	—	—	—	11,900	110	99.1	—	—	—	34.4	6.5	81.1
Hg	—	—	—	6,040	150	97.5	—	—	—	—	—	—
Hg	—	—	—	67	1.5	97.8	—	—	—	—	—	—
As	—	—	—	135	19	85.9	—	—	—	—	—	—
Ni	—	—	—	—	—	—	—	—	—	3.6	2.1	43.1

^a Source: Reference 4. ^b Source: Reference 5. ^c Source: Reference 6. ^d Source: Reference 7.

TABLE 5. OTHER SITE REMEDIATION OPERATIONS VISITED BY ALLIANCE/EPA FIELD TEAM IN MARCH 1988 IN THE NETHERLANDS AND THE FEDERAL REPUBLIC OF GERMANY

Company Institution	Technology	Pollutants treated	Medium treated	Principal Operators	Scale of system	Size and time of treatment	Treatment costs	Capital costs
TNO-Dept. of Environmental Technology Delft, the Netherlands.	Electrochemical Dechlorination Treatment	Polar and Ionic Organohalogenes	Dilute Aqueous Waste Streams	<ul style="list-style-type: none"> • Titanium anode • Woven carbon fiber cathode • Membrane between • Surface active additives • About 10 A, 60 mins. 	Bench	Pilot tests will be 26 gal/hr	\$0.02/gal	Not yet determined
TNO- Dept. of Process Technology Apeldoorn, the Netherlands.	Bioreactors	Non-chlorinated hydrocarbons	Slurried or dry soil	<ul style="list-style-type: none"> • Mixing and aeration • Nutrients • Detergents • Native microorganisms 	Bench	Pilot tests will be 11 tons/day	\$45/ton	Not yet determined
RIVM- Soil and Ground Water Research Laboratory Bilthoven, the Netherlands.	<i>In Situ</i> Biorestation	Gasoline	Soil	<ul style="list-style-type: none"> • Infiltration of nutrients • Water • H₂O₂ as oxygen source • Iron extraction unit 	Full	1961 cu yds. 1½ years	\$171/cu yd	\$336,000
TAUW infra Consult by Deventer, the Netherlands.	<i>In Situ</i> Cadmium Removal	Cadmium	Soil	<ul style="list-style-type: none"> • Infiltration of acidic water to leach cadmium (pH = 3.5) • Ion exchange onsite 	Full	39,200 cu yds., 1 year	\$63/cu yd	\$2.5 million
TAUW Infra Consult by Deventer, the Netherlands.	Rotating Biological Contactors	Pesticides	Ground Water	<ul style="list-style-type: none"> • Metal honeycomb disks • Compost air filter • Sand filtration • Activated carbon 	Full	110 gpm	Data not available	Data not available—total costs reduced 30% with RBC
Hannover Umwelt-technik GmbH Waldorf, FRG	<i>In Situ</i> Vacuum Extraction and Air Stripping	Volatile organics	Soil vadose zones and ground water	<ul style="list-style-type: none"> • PVC slotted wells extract from vadose • Small pump • Activated carbon column • Compressed air injected into ground water 	Full	About 10,000 cu yds, 1 year	<\$5/ton	\$1500, depending on scale of project
Unweltschutz Nord GmbH Ganderkesee, FRG	On-site Composting	Non-Chlorinated hydrocarbons	Soils	<ul style="list-style-type: none"> • Unique substrate • Nutrients, microbes • PET liner with leachate collection • Aeration • Greenhouse cover 	Full	131 cu yds per bed, 6 months with greenhouse	\$90/ton	Varies

charged metal ions that occurs when the ground is electrically charged by insertion of one or more electrode arrays. Electroreclamation can be applied *in situ*, on-site, or off-site, and can also be used to "fence off" hazardous waste sites or potentially hazardous industrial sites [8].

With approximately 70 percent of the participants from industry, the conference provided an opportunity for EPA Regional staff, clean-up contractors, and vendors to make contacts and to discuss the advantages and limitations of innovative technologies in order to make better choices among technologies under consideration at Superfund sites.

CONCLUSIONS AND RECOMMENDATIONS

Soil washing experience in the Netherlands and the FRG has shown that soil washing can be conducted on a large scale at costs substantially lower than those of incineration (with notably less effectiveness). Although most of the technologies generate 10 to 20 percent of the initial volume as sludge, work is being conducted in the FRG to improve effectiveness of soil washing on fine materials and to reduce sludge generation. Typical cleaning efficiencies for soil washers ranged from 75 to 95 percent removal, depending on the contaminant. Although the au-

thors believe that soil washing technologies could be used effectively in the United States to significantly reduce landfilling of CERCLA site soils, it is unlikely that domestic or foreign companies will invest in this market unless a uniform set of soil cleanup criteria are developed or technology-based criteria are established.

Biological treatment technologies have been shown to be useful both for polishing to lower concentrations using *in situ* treatment, and for gross removals of organic materials using rotating biological contactors and composting systems. Efforts should be made to encourage the use of these types of systems in the United States.

In situ vacuum extraction of volatile organic compounds is a well-known technology in the United States. Applications in the FRG include the use of *in situ* air stripping of volatiles from ground water into the vadose zone and their subsequent removal by the extraction wells. Such vacuum extraction applications and other innovations such as bioaugmentation should be encouraged in the United States.

The apparent success of this short-duration technology assessment program indicates that despite the wealth of information available in the United States, there is much to be learned from ongoing work in foreign countries. Several attendees at the Phase III international forum expressed surprise at the advanced state of waste treatment

in Europe and that some techniques, such as innovative application of vacuum extraction, are considered standard in Europe while still under scrutiny domestically. The authors recommend that further efforts be made to encourage the transfer of European site remediation technologies through improved literature dissemination and seminar presentations at symposia. The enthusiastic response from participants of the international forum to these European technologies has sparked talk of making the forum an annual event, with further outreach efforts to identify innovative technologies on other continents.

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Performance Models for NO_x Absorbers/Strippers

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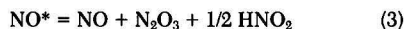
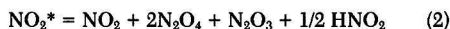
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The focus of this paper is to present a review of recent developments in the modeling of NO_x absorbers and strippers. The fundamental concepts of design and process simulation for this specialized area of mass transfer are developed. This review and conceptual analysis is intended to provide simple design/simulation equations and to present the usefulness and limitations of these equations. This activity is useful because of the interrelationships between mass transfer and the complexity of the NO_x-HNO₃-H₂O chemical system.

INTRODUCTION

The abatement of nitrogen oxides is a significant industrial concern. Gaseous nitrogen oxides arise from such sources as the production and storage of nitric acid, nitrogenation reactions, metal plating and finishing, and metal dissolution. The purpose of this paper is to update the reader as to recent advancements in the understanding of nitrogen oxide (NO_x) scrubbing and stripping operations as well as other relevant phenomena. Emphasis is placed on the development of fundamentally sound approaches to the design and simulation of both packed and plate scrubber devices. The choice between packed- and plate-type scrubbers is a matter of economics. Generally plate devices are preferred where recovery of the NO_x is intended to result in the production of an aqueous HNO₃ product; such recovery often results in the production of gaseous NO and significant heat generation which are more easily handled in plate-type scrubbers. For stripping of NO_x gases from nitric acid solutions, plate-type devices are preferred for low concentration nitric acid solutions while packed towers are suitable for more concentrated nitric acid solutions. Gaseous nitrogen oxides occur in all the positive oxidation states of nitrogen. To simplify

the following discussion involving gaseous species, nitrogen oxide (NO_x), "chemical" nitrogen dioxide (NO₂^{*}) and chemical nitrogen oxide (NO^{*}) are defined as

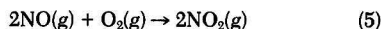


Analytical results and general discussions are usually based on chemical NO_x, NO₂^{*}, and NO^{*} components.

Much of the published information about nitrogen oxide scrubbing comes from the nitric acid production industry. At conditions existing in the usual nitric acid production tower [1], the descriptive chemical equations are

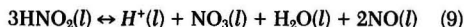
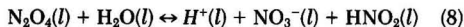
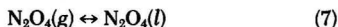
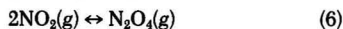


and



From these overall chemical equations, it may be seen that the absorption and reaction of NO₂ and water pro-

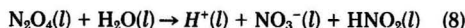
duces NO, which desorbs to the gas phase. Provided that the gas phase residence time is adequate, NO may be oxidized in the gas phase and reabsorbed as NO₂. It is helpful to further study Equation (4) to gain insight to this overall reaction. Equation (4) may be broken down to



In this scheme of equations, NO₂ and N₂O₄ are assumed to be in continuous gas phase equilibrium [2]. The solubility of NO₂ is neglected because it is much less than N₂O₄ [3] and also because N₂O₄ is much more reactive with water than NO₂ [4]. Counce and Perona [5, 6] used this scheme of reactions to model the absorption of a concentrated gas mixture of NO₂-N₂O₄ in a sieve plate tower. In their work, the concentrations of HNO₃ and HNO₂ acids were sufficiently dilute so that Equation (8) was treated as irreversible. The significance of equation sequence 6 through 10 is illustrated in some data adapted from the work of Makhotkin and Shamsutidinov [7] presented in Figure 1. In this semibatch experiment, 1% NO₂* in N₂ was bubbled through water. The resulting concentration profiles and ratios show that the ratio of NO* produced to NO₂* absorbed reaches 1:3 only when a semi-steady state concentration of HNO₂ is established. This is important in scrubber design and results from the kinetic and mass transfer limitations of the aqueous decomposition of HNO₂ [8] requiring a substantial HNO₂ concentration for a driving force. If this concentration driving force is not established during scrubbing, the ratio of NO* produced to NO₂* absorbed may be very much less than 1:3. For example, this ratio is likely to be 1:3 in plate-type absorbers which normally feature long liquid phase residence times and less than 1:3 for packed absorbers which feature short liquid phase residence times.

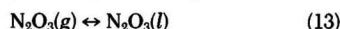
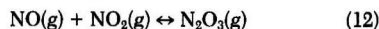
The aqueous products from reactions of NO₂ and water are largely HNO₂ and HNO₃ for solutions of <50 wt% of HNO₃; for higher concentrations of HNO₃, the reaction products are largely N₂O₄ and HNO₃. The non-HNO₃ liquid species are more easily removed from solution than HNO₃ and their removal is often necessary. The removal of HNO₂ from aqueous solutions is linked to the desorption of NO from solution, which allows the reaction expressed in Equation 9 to proceed, and due to the physical

desorption of HNO₂. The overall decomposition reaction of Equation 9 may be broken down to

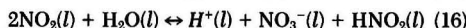


The rate controlling step here is either the desorption of NO or the hydrolysis of N₂O₄.

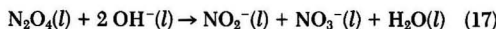
The absorption of N₂O₄ tends to be the dominant absorption route, at least at moderate to high NO₂* partial pressures, however, other species such as N₂O₃ may be important in water scrubbing of NO₂ gas mixtures with high NO* to NO₂* ratios, especially at low NO₂* partial pressures [9]. This absorption route is represented by



At extremely low NO₂* partial pressures and in the absence of NO* the absorption of N₂O₄ becomes less important and the absorption of NO₂ is the predominant absorption route [8, 10, 11]. This absorption route is represented as



When aqueous caustic scrub solutions are used, additional liquid-phase reactions will take place; the primary reactions may be represented as [8, 12]



and



The increase in solution reactivity for N₂O₄ absorption into caustic solutions appears to largely be offset by the decrease in solution solubility; this does not appear to be the case for N₂O₃ absorption into caustic solutions. Aoki *et al.* [12] observed large increases in the absorption rate of NO₂*-NO* gas mixtures when caustic solutions were used as the absorbent rather than water alone; they attributed this increase to the dramatically increased flux of N₂O₃. Recent studies on the absorption of NO*-NO₂* gas mixtures into 24 wt% NaOH solutions by Newman and Carta [13] concluded that HNO₂ is an absorbing specie; however, this phenomena appears to be only important for scrubber design in cases of devices with extremely long gas phase residence times.

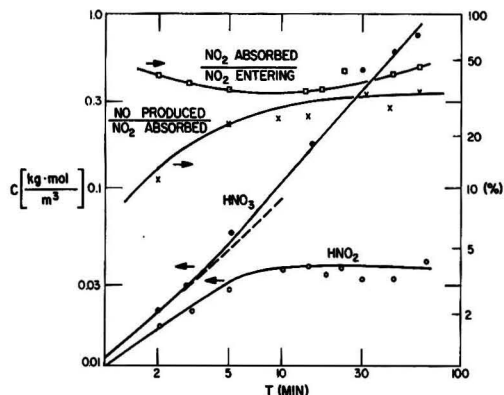


Figure 1. Results of semibatch NO₂ absorption studies. Adapted from A. F. Makhotkin and A. M. Shamsutidinov, *Khim. Khim. Tekhn.* XIX (1976).

MATHEMATICAL MODELS

The key concept in the following presentation is that of the absorption flux. In general, the absorption flux may be represented for component A as

$$R_A = k_C(P_A - P_A^*) = Ek_L(C_A^* - C_A) \quad (19)$$

Important nitrogen oxide species for aqueous absorption are NO* and NO₂*; the absorption flux of NO* may be represented as

$$R_{\text{NO}^*} = R_{\text{NO}} + R_{\text{N}_2\text{O}_3} \quad (20)$$

and that of NO₂* as

$$R_{\text{NO}_2^*} = 2R_{\text{N}_2\text{O}_4} + R_{\text{N}_2\text{O}_3} + R_{\text{NO}_2} \quad (21)$$

These NO* and NO₂* absorption fluxes may be related to differential mass balances by

$$G dY_{\text{NO}_2^*} = R_{\text{NO}_2^*} adZ \quad (22)$$

$$G dY_{NO^*} = R_{NO^*} adZ \quad (23)$$

The overall differential balance for NO_x is then

$$G dY_{NO_x} = (R_{NO_x^*} + R_{NO^*}) adZ \quad (24)$$

The aqueous absorption of NO_x species is accompanied by simultaneous hydrolysis reactions; for absorption in industrial-type contactors the absorption of N_2O_4 and N_2O_3 into water and dilute nitric acid usually occurs in the "fast pseudo first-order reaction regime" [14]. The absorption of component A when accompanied by a fast pseudo first-order liquid phase chemical reaction with component B may be described as

$$R_A = k_C (P_A - P_A^*) = (\sqrt{Dk}/H)_A P_A^* \quad (25)$$

From observation of Equations (19) and (25) it may be noted that

$$H_A = P_A^*/C_A^* \quad (26)$$

and

$$(E)_A = (\sqrt{Dk}/k_L)_A \quad (27)$$

restrictions here are that

$$3 < E < 1 + D_B C_B / D_A C_A^* \quad (28)$$

Where O_2 is present, the oxidation of NO may be important,

$$-r_5 = k_5 P_{NO}^2 P_{O_2} \quad (29)$$

General equations for the absorption flux of NO_x into aqueous solutions for many industrial applications are [9]

$$G d(P_{NO_2^*}/\pi) = \{[2(\sqrt{Dk}/H)_{N_2O_4} P_{N_2O_4} + (\sqrt{Dk}/H)_{N_2O_3} P_{N_2O_3} + k_L P_{NO_2^*}/H_{NO_2}]\} a - (-r_5 \epsilon) \} dZ \quad (30)$$

$$G d(P_{NO^*}/\pi) = \{[(\sqrt{Dk}/H)_{N_2O_3} P_{N_2O_3} + k_L (P_{NO}/H_{NO} - C_{NO})]\} a + (-r_5 \epsilon) \} dZ \quad (31)$$

Nitric oxide, NO , is produced in the liquid phase by the decomposition of HNO_2 as shown in Equation 9. The bulk phase concentration of NO may be estimated by

$$C_{NO} = \left[\frac{K_9 C_{HNO_2}^3}{C_{H^+} C_{NO_3^-}} \right]^{1/2} \quad (32)$$

The maximum possible flux for the bulk phase decomposition of HNO_2 is given by Crawford and Counce [15] as

$$(-R_{NO})_{max} = 2/3 (-r_9) \epsilon_L / a \quad (33)$$

where

$$-r_9 = (3K_L a / 2\epsilon_L)^{2/3} (k_9 / H_{NO_2}^2)^{1/3} (C_{HNO_2})^{4/3} \quad (34)$$

The overall absorption flux of NO_x may then be described as

$$G d(P_{NO_x^*}/\pi) = G d(P_{NO_2^*}/\pi) + G d(P_{NO^*}/\pi) \quad (35)$$

The differential mass balances for NO^* and NO_2^* are predicated on the assumption that primary mass-transfer resistance is in the liquid phase. Calculation of the total gas and liquid phase resistances for NO_x absorption is not necessary for many applications; the assumption of dominant liquid phase resistance may be checked by comparing the maximum liquid phase flux with that of the gas phase.

The removal of HNO_2 from solutions was found to be largely due to the bulk phase decomposition of HNO_2 as well as the physical desorption of HNO_2 by Crawford and Counce [15]. For nitric acid solutions of less than 50 wt%, the predominate NO_x - HNO_x specie other than HNO_3 is HNO_2 . The removal of these NO_x - HNO_x species other

than HNO_3 is often prerequisite to concentration of these acid solutions by distillation. Such operations may be modeled as

$$L dC_{HNO_2} = (\Phi_1 + \Phi_2) \quad (36)$$

where

$$\Phi_1 = (-r_9) \epsilon_L S dZ \quad (37)$$

and

$$\Phi_2 = K_L a (P_{HNO_2}/H_{HNO_2} - C_{HNO_2}) S dZ \quad (38)$$

The production of NO due to the decomposition of HNO_2 may be largely avoided by scrubbing NO_x gases with caustic solutions. The problem of absorber modeling is then one of predicting the enhancement factors for N_2O_4 and N_2O_3 absorption. Little is known about any enhancement of NO_x absorption. Provided that the criteria for the fast reaction regime are met, the \sqrt{Dk}/H parameters may be utilized here; the "k" term in this expression may be visualized as

$$k = k_8 C_{H_2O} + k_{17} C_{OH^-} \quad (39)$$

for N_2O_4 reaction, and

$$k = k_{14} C_{H_2O} + k_{18} C_{OH^-} \quad (40)$$

for N_2O_3 absorption. The Henry's coefficients will also increase as the ionic strength of the solution changes from that of water.

Application of Mathematical Models

The model expressed in Equations 30 and 31 is essentially that verified by Counce and Perona [16] in experiments with a 0.102 m-ID column packed with 1.27 cm Intalox saddles. This model is used to illustrate the effects of several phenomena. This effect of the NO_x oxidation state is investigated in Figure 2; this figure shows the importance of this parameter on NO_x removal efficiency for

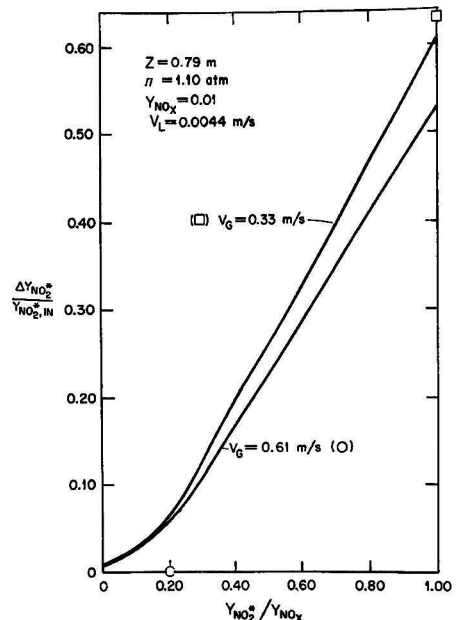


Figure 2. Model predicted and experimental NO_x removal efficiency in an atmospheric pressure water scrubber packed with 13 mm Intalox saddles.

some NO_x absorption studies with packed towers [16]. The relative importance of the absorption mechanisms for the prediction of Figure 2 [9] for the lower gas velocity is shown in Figure 3 [9]. The parameter Φ_i is an indicator of the importance of a particular absorption route (i.e., Φ_{NO₂} is the total molar absorption of NO₂ divided by the total NO_x absorption of the tower for particular parameter settings),

$$\Phi_i = \frac{R_{i,T}}{\sum R_{i,T}} \quad (41)$$

Inspection of Figure 3 shows that most of the NO_x absorbed at high oxidation levels of the feed gas occurs by the absorption of N₂O₄. At lower oxidation levels in the feed gas, the N₂O₃ absorption route becomes more important. The absorption of NO₂ is of negligible importance for these predictions. At higher NO₂* partial pressures and similar NO₂*/NO_x ratios the dominance of the N₂O₄ absorption route increases; the reverse is true at lower NO₂* partial pressures.

Selby and Counce [11] investigated the absorption of dilute NO₂-N₂O₄ gases in air into water at atmospheric pressure using a 0.102-m ID column with commercial plastic gauze packing (Koch-Sulzer Type BX). The fraction of the NO₂-N₂O₄ absorption due to the N₂O₄ mechanism was estimated to be 84%, 50% and 30% at NO₂* partial pressures of 0.0010, 0.00023 and 0.0001 atm. Little or no liquid phase HNO₂ decomposition was detected and little gas phase resistance was present. Their model for NO₂* absorption is based on a simplification of Equation 30,

$$G d(P_{NO_2^*}/\pi) = [2Ek_L/H_{N_2O_4} P_{N_2O_4} + k_L P_{NO_2^*}/H_{NO_2}] a dZ \quad (42)$$

which was integrated to the form

$$\ln \frac{A + BY_{NO_2^*,out}}{Y_{NO_2^*,out}} - \ln \frac{A + BY_{NO_2^*,in}}{Y_{NO_2^*,in}} = AaZ \quad (43)$$

where

$$A = k_L \pi / G H_{NO_2} \quad (44)$$

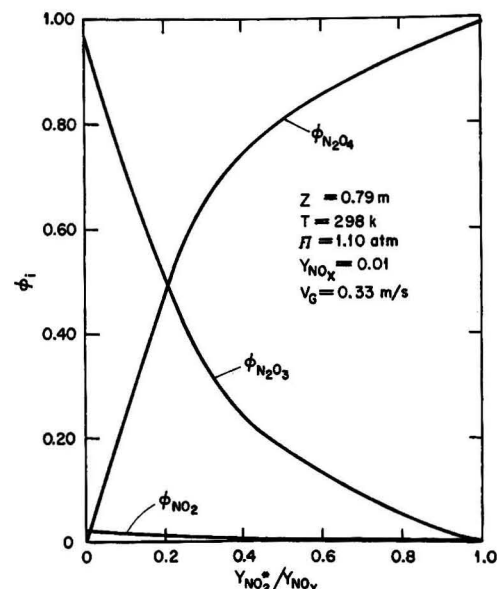


Figure 3. Relative importance of removal mechanisms for the indicated conditions. The gas velocity is the lower of the two from Figure 2.

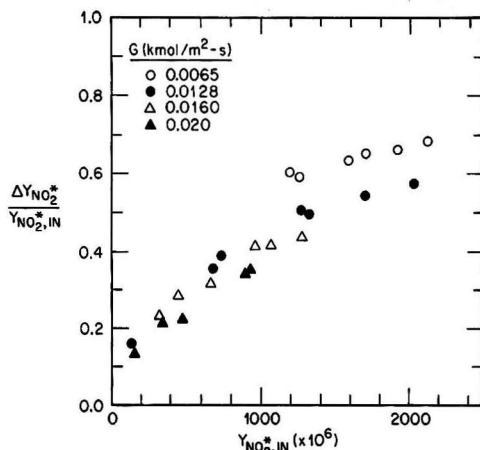


Figure 4. NO₂* conversion versus inlet NO₂* mole fraction at various gas rates. These mole fractions have been multiplied by 10⁶. Reprinted from *Ind. Eng. Chem. Res.*, 27, 1917-22, Copyright 1988 American Chemical Society.

and

$$B = 2(Ek_L/H)_{N_2O_4} K_6 \pi^2 / G \quad (45)$$

Their data are shown in Figure 4. Their model (Equation 43) agrees very well with the data as shown in Figure 5.

At sufficiently high NO₂* concentrations, the absorption of NO₂ may be neglected. A further simplification of Equation 30 for conditions of no N₂O₃ or NO₂ absorption yields

$$G dY_{NO_2^*} = 2(\sqrt{Dk}/H)_{N_2O_4} \pi Y_{NO_2^*} a dZ \quad (46)$$

For reasonably dilute NO₂* gases where

$$Y_{NO_2} \approx Y_{NO_2^*} \quad (47)$$

Equation 44 may be integrated to yield

$$1/Y_{NO_2^*,out} - 1/Y_{NO_2^*,in} = 2(\sqrt{Dk}/H)_{N_2O_4} \pi^2 K_6 a' / G \quad (48)$$

Equation 48 is compared with data on the absorption of NO₂-N₂O₄ gases in a single-tray bubble-cap tower [17] in Figure 6. Again, rather good agreement is noted. Values of $(\sqrt{Dk}/H)_{N_2O_4}$ and K₆ are as recommended by Hoftyzer and Kwanten [1]. The value of a' is as recommended by Sharma *et al.* [18].

The stripping of NO_x-HNO_x species other than HNO₃ was investigated by Crawford and Counce [15]; the primary specie of concern was HNO₂. Their work was done

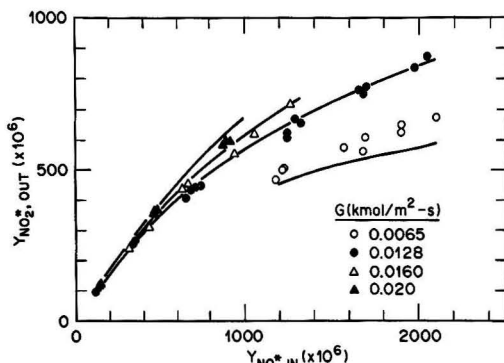


Figure 5. Inlet NO₂* mole fraction versus experimental and model predicted outlet NO₂* mole fraction at various gas rates. Reprinted from *Ind. Eng. Chem. Res.*, 27, 1917-22 (1988).

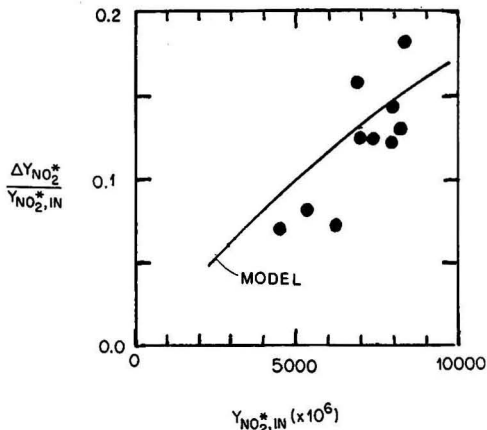


Figure 6. Comparison and experimental and model predicted conversion of NO_2^* in a single-plate bubble-cap column. Data from Peters *et al.* *AIChE J.*, 1, (1) 105 (1955).

at atmospheric pressure and with low HNO_3 concentrations in columns packed with 0.64 and 1.27 cm Intalox saddles. The simpler of their approaches to describing the removal of HNO_2 in packed towers is

$$L(C_{\text{HNO}_2,\text{in}} - C_{\text{HNO}_2,\text{out}}) = \Phi_T = \Phi_{1,m} + \Phi_{2,m} \quad (49)$$

where

$$\Phi_{1,m} = (-r_9)_m \epsilon_L SZ \quad (50)$$

and

$$\Phi_{2,m} = K_L a (P_{\text{HNO}_2}/H_{\text{HNO}_2} - C_{\text{HNO}_2})_m SZ \quad (51)$$

A comparison of model results as experimental data presented in Figure 7 indicates good model/data agreement. At the conditions of Figure 7, approximately 1/3 of the depletion was due to the physical desorption of HNO_2 (Φ_2) and 2/3 due to the liquid-phase decomposition of HNO_2 (Φ_1).

The use of caustic scrub solutions can prevent the production of NO in the scrubbing process and allows recy-

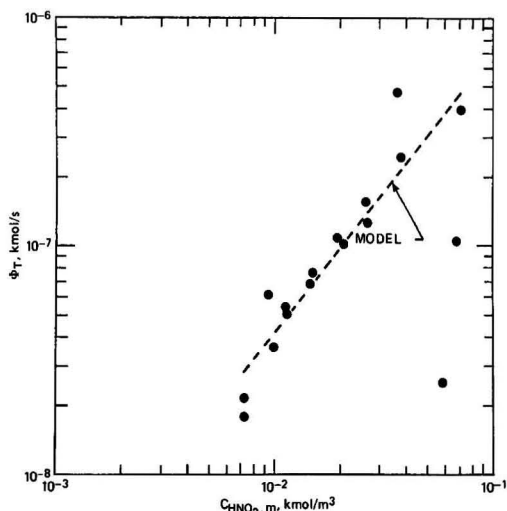


Figure 7. A comparison of experimental and model predicted values of Φ_T vs mean HNO_2 concentration; these studies utilized a 0.102-m-ID column packed with 1.27-cm Intalox saddles. Reprinted from *Sep. Sci. Tech.*, 23 (12 & 13) 1573 (1981) Courtesy of Marcel Dekker Inc.

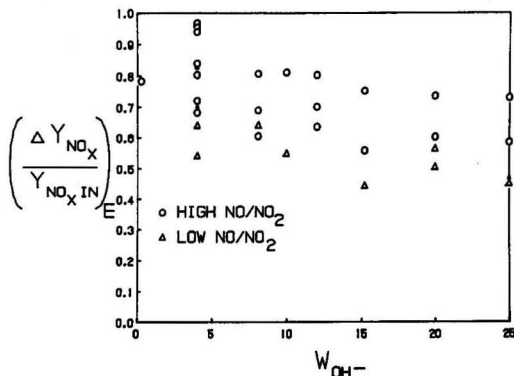


Figure 8. Experimental NO_x absorption results from studies at atmospheric pressure with 0.102-m-ID column packed with 1.27-cm Intalox saddles.

cle of the scrub solutions. The use of caustic scrub solutions enhances the N_2O_3 absorption route and allows for more efficient scrubbing of $\text{NO}_2^*-\text{NO}^*$ gases than with water alone. This phenomena may be seen in Figure 8 which shows greater experimental removal efficiencies for gases with higher $\text{NO}^*/\text{NO}_2^*$ ratios; this improvement would not be expected when the $\text{NO}^*/\text{NO}_2^*$ ratio exceeds unity. Lucero *et al.* [19] developed a model based on N_2O_4 and N_2O_3 absorption to describe the absorption of $\text{NO}_2^*-\text{NO}^*$ gas, mixtures into caustic scrub solutions,

$$G dY_{\text{NO}_2^*} = [2(\sqrt{Dk}/H)_{\text{N}_2\text{O}_4} P_{\text{N}_2\text{O}_4} + (\sqrt{Dk}/H)_{\text{N}_2\text{O}_3} P_{\text{N}_2\text{O}_3}] aZ \quad (52)$$

and

$$G dY_{\text{NO}^*} = (\sqrt{Dk}/H)_{\text{N}_2\text{O}_3} P_{\text{N}_2\text{O}_3} aZ \quad (53)$$

A comparison of model and data in Figure 8 indicates good model-data agreement. The gas-liquid interfacial area is calculated from correlations for flexirings and Intalox saddles by Joshi *et al.*, [20]. The gas-liquid interfacial area for the Koch Sulzer packing was taken to be the geometric area, 450 m^{-1} [21]. Lucero *et al.*, [19] present an approximation for the effect of OH^- concentration on the $(\sqrt{Dk}/H)_{\text{N}_2\text{O}_4}$ parameter ($\text{kg mol}^{-1/2} \text{ atm}$)

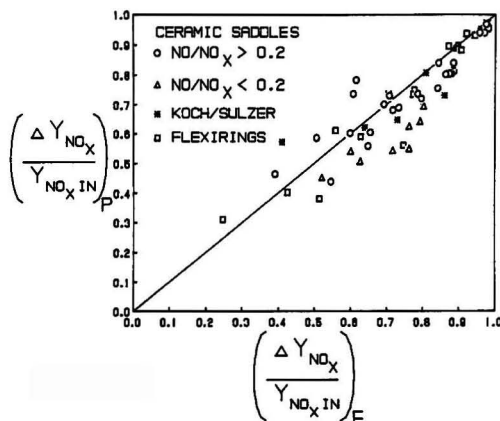


Figure 9. Comparison of model predicted versus experimental NO_x absorption results from studies with 0.102-m-ID column packed with 1.27-cm ceramic Intalox saddles, Type BX Koch plastic Sulzer Packing and 1.6 cm plastic flexirings at atmospheric pressure.

$$(\sqrt{Dk/H})_{\text{NO}_2} = 7.8 \times 10^{-4} - 1.365 \times 10^{-5} \omega_{\text{OH}^-} \quad (54)$$

This approximation is based on data with 1.27 cm ceramic Intalox saddles. The value of the $(\sqrt{Dk/H})_{\text{NO}_2}$ parameter is that obtained by Aoki *et al.* [12]. The data used for comparison in Figures 8 and 9 are from experiments conducted at the Research Triangle Institute.

CONCLUSIONS

The models presented here show reasonable agreement with various aspects of NO_x - HNO_x absorption and stripping concerns. Much of the uncertainty in the use of the approaches presented here is in determination of the appropriate models for interfacial area and mass-transfer coefficients for industrial contactors. These models may, however, be used for alternative comparison in process design activities and provide reasonable approximations for equipment selection—provided the constraints and assumptions of the various equations are observed. Further studies are needed to determine the mechanism of absorption of NO_2^* into caustic solutions at low NO_2^* mole fractions, and to elucidate the roles of N_2O_3 and HNO_2 in the absorption of NO^* - NO_2^* gas mixtures into caustic solutions.

NOTATION

a'	= interfacial area per tower cross sectional area
a	= interfacial area per volume of tower
C_i	= concentration
D	= diffusion coefficient
E	= enhancement factor
g	= gas
G	= molar velocity of all gas
H	= phase distribution coefficient for component i , $H_i = P_i/C_i$
k	= first order reaction rate constant
k_i	= reaction rate constant for reaction i
k_G	= gas-phase mass-transfer coefficient
k_L	= liquid-phase mass-transfer coefficient
K_L	= overall liquid-phase mass-transfer coefficient
K_i	= pressure equilibrium constant of reaction i for the stoichiometry as written
l	= liquid
L	= volumetric liquid flow rate
P_A	= partial pressure of component A
P_T	= total pressure
R_j	= absorption rate per interfacial area for component j
S	= cross sectional area
V_G	= gas velocity
V_L	= liquid velocity
ω_{OH^-}	= weight percent OH^-
X_A	= conversion of component A also $\Delta Y_A/Y_{Ain}$ in
y_A	= P_A/π , mol fraction of A in gas
Z	= height
ϵ	= void fraction
ϵ_L	= liquid holdup
π	= total pressure
Φ	= depletion rate for HNO_2 depletion rate studies or indicator of importance of various absorption routes for NO_x absorption

Superscript

* = interfacial

Subscripts

i	= interfacial
in	= entering
m	= mean
out	= exiting

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Estimation of Multimedia Environmental Contamination of 2,3,7,8-TCDD Emissions from Municipal Waste Incinerators

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2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is known to be most toxic among congeners of polychlorinated dibenzo-p-dioxins (CDD), and is known to cause cancer to humans upon prolonged exposure—even at extremely low dosage. The municipal waste incinerator is one of the combustion devices where literature test results have shown the presence of 2,3,7,8-TCDD or CDDs in flue gas or ash. A recent report compiled by the U.S. Environmental Protection Agency [13] also lists other combustion devices such as smelters, sewage sludge incinerators, wire reclamation incinerators, and drum and barrel furnaces. In addition, Sheffield [11] mentions forest fires and several types of chemical production facilities as sources. Des Rosier and Lee [2] cite PCB transformer fires as a potential source of 2,3,7,8-TCDD formation. The primary focus of this paper is to present the potential of environmental contamination due to emissions of 2,3,7,8-TCDD and disposal of fly ash generated from the incineration of municipal waste. Example assessments for municipal incinerators presented in this paper are based on presently available estimation techniques and hence represent estimates for environmental concentrations, exposures and health risks. Although actual emission data are used, uncertainties associated with the estimates cannot be fully assessed until these estimates are compared with some monitoring data, especially concerning environmental concentrations related to indirect exposure pathways.

INTRODUCTION

The available literature information on emission tests shows that 2,3,7,8-TCDD emissions released into the atmosphere consist of vapors and particulate matter. Although the exact ratio of vapor to particulate 2,3,7,8-TCDD emissions has not been systematically studied, the mere presence of the two-phase releases is worth noting and complicates the analysis of environmental contamination. There is an indication that the long-range transport of 2,3,7,8-TCDD favors the presence of 2,3,7,8-TCDD in the vapor phase [3].

Human exposure can result directly from inhaling vapor and particulate forms of 2,3,7,8-TCDD. Indirectly, the routes of exposure can include ingestion of contaminated water, fish, soil and homegrown food, and dermal contact.

Ash is produced from non-combustible material as bottom ash, and from the remains of the refuse and fuel after burning airborne fly ash which is collected in particulate control equipment. The bottom ash, which is not the material collected from the airborne fly ash, is often called slag. Nottrodt [8] and Hay, *et al.* [5] indicate that the total CDD bottom ash slag is negligible. MRI [6] reports levels of 2,3,7,8-TCDD in bottom ash as high as 1.5 ng/g. However, the bottom ash used in the MRI report refers to a mixture of both bottom and fly ash, and it is not shown how much of 2,3,7,8-TCDD comes from the bottom ash. Due to this uncertainty, and since literature information indicates that fly ash is of greater concern than bottom ash in terms of the presence of 2,3,7,8-TCDD, in this paper slag is not considered in evaluating environmental contamination resulting from land disposal of fly ash.

INCINERATOR SCENARIOS

This paper addresses four scenarios based on environmental settings and types of incinerators. Two of the scenarios (1 and 2) assume population habits which involve cultivation of some farm products and a stagnant pond stocked with fish. These two scenarios refer to incinerators at different locations and with different emission rates. The other two scenarios (3 and 4) assume habits which also involve obtaining some farm products from the impact area, but have a stream near the incinerator. It is assumed that fish can survive in the flowing streams. Of the four scenarios, two (scenarios 1 and 3) deal with a large, 3000 TPD capacity incinerator, while the other two (scenarios 2 and 4) deal with a smaller, 120 TPD facility. The major assumptions for the incinerator facilities, including incineration parameters and emission factors, are summarized in Table 1. Population habits in the affected area are assumed to be similar in all four scenarios.

The affected receptors include a hypothetical family near the municipal waste incinerator. Buildings assumed for scenarios 2 and 4 cause plume downwash effects which cause the modeled maximum concentrations in the air to occur 200 m from the incinerator. Since the hypothetical family is assumed to live on a small farm it is unreasonable to expect them to be located in the urban area where the ground level concentrations are maximum. The nearest distance where a small farm could be located was assumed to be about 0.5 miles from the incinerator. For this reason the hypothetical family is located 0.5 miles (0.8 km) from the incinerator. Environmental concentrations and corresponding exposures are estimated for the receptors located at this distance.

EMISSION DATA

Since the major emphasis of this paper is to assess environmental contamination of 2,3,7,8-TCDD, emissions data for other types of CDDs are not emphasized in this paper. Many of those references which do not contain specific analyses for 2,3,7,8-TCDD are omitted from the emission data base.

In attempting to quantify the presence of CDD emissions in flue gas, researchers primarily analyzed fly ash emissions. Although some papers reported measured emissions for vapor phase as well as particulate CDDs in flue gas, most literature does not distinguish between the two.

TABLE 1. PARAMETER VALUES FOR INCINERATOR FACILITIES IN SCENARIOS 1-4

	Scenarios	
	1 & 3	2 & 4
Capacity(TPD)	3000	120
Building Height(m)	42	27.3
Controlled Emission Factor for 2,3,7,8-TCDD ($\mu\text{g}/\text{kg}$)	0.001	0.289
Emission Rate for 2,3,7,8-TCDD(g/s)	3×10^{-8}	1.1×10^{-7}
Vapor Form Emission Rate (g/s)	1.9×10^{-8}	1.1×10^{-7}
Particulate Form Emission Rate (g/s)	1.1×10^{-8}	0.7×10^{-7}
Number of Stacks	4	2
Stack Height(m)	46	27.4
Stack Diameter	4.1	1.2
Stack Gas Temperature ($^{\circ}\text{K}$)	470	543
Stack Gas Velocity (m/s)	11.3	12

In several emission tests, the levels of 2,3,7,8-TCDD in the gas phase were higher than those measured on captured particulate matter [4, 7, 10, 15]. In one study testing a municipal incinerator, virtually all CDD emissions in the stack were in the gas phase [15].

More recently, Midwest Research Institute, under contract to the EPA, summarized an emission data base for stack test results conducted in United States and Canada [16]. The results show analyses of various congeners of dioxins in stack emissions, but there is no indication as to what proportion is particulate versus vapor form. Knowledge of the relative amounts of particulates and vapors in stack emissions is important because in the environment vapors will behave differently from particulates.

Scenarios 2 and 4 present a facility with relatively poor control of 2,3,7,8-TCDD emissions, while scenarios 1 and 3 present a facility with fairly well-controlled 2,3,7,8-TCDD emissions. It should be noted, however, that the emission factor used for scenarios 1 and 3 does not reflect data for facilities with state-of-the-art control technologies in regard to 2,3,7,8-TCDD emissions.

While no test data concerning the division of 2,3,7,8-TCDD emissions between the vapor and particulate phases for stack emissions at facilities in the U.S. could be located, three European studies analyzing the vapor and particulate phase emissions from a municipal waste incinerator were found [4, 7, 10]. Nielsen, *et al.* [7] states that the reported distribution of CDDs between particulate and vapor phases varies widely, but it is generally recognized that an average of 20%-30% is in the particulate phase, while 70%-80% is in the gas phase. In the assessment shown later it is assumed that 63% of the total 2,3,7,8-TCDD emissions is in the vapor phase and 37% particulate, since these values are reported in two studies [4, 10].

For all four scenarios, the heights of the buildings are assumed to be as tall as the stack heights. This triggers the building downwash effects in the application of air dispersion modeling. The air dispersion calculations used here incorporate a simulation of precipitation along with building downwash caused by a short stack height [14]. The results of a sample dispersion modeling can be found in U.S. EPA [14]. In this report the deposition rate of particulate matter and the ambient air concentration of various pollutants emitted at a given rate are given as a function of distance and the sector of the area.

The particle distribution is needed to estimate the deposition rate of particulate matter, because the settling velocity is a function of particle size and density. The particle size distribution assumed for air dispersion modeling which incorporates the dry and wet deposition is 6.7% for particles greater than 10 μm in diameter, 26.7% for particles between 2 and 10 μm in diameter, and 66.6% for particles less than 2 μm in diameter.

The deposition rates for particulate-form 2,3,7,8-TCDD and the ambient air concentrations of vapor-form and particulate-form 2,3,7,8-TCDD in the surrounding area are based on the air dispersion modeling, and their estimates are shown for the locations where the maximum deposition and concentration are likely to occur (200 m) and where the populations in the scenarios are assumed to be at 0.8 km from the incinerator. Local meteorological conditions are incorporated in the dispersion calculations.

SOIL CONTAMINATION

In addition to human exposure to 2,3,7,8-TCDD resulting from breathing it in the air, human exposure can result from soil contaminated by the fallout of particulate phase emissions and adsorption of the vapor phase

TABLE 2. ESTIMATED AIR CONCENTRATION AND DEPOSITION RATE FOR SCENARIOS 1-4

	Max. Conc. at 200m (g/m ³)	Max. Deposition Rate (μg/m ² · yr)	Conc. at 0.8 Km (g/m ³)	Deposition Rate at 0.8 Km (μg/m ² · yr)
Vapor-Form 2,3,7,8-TCDD (3000 TPD)	2.1×10^{-15}		1×10^{-15}	
Particulate-Form 2,3,7,8 (3000 TPD)	1.2×10^{-15}	3.7×10^{-8}	6.5×10^{-16}	6.3×10^{-4}
Vapor-Form 2,3,7,8-TCDD (120 TPD)	1.8×10^{-13}		8.3×10^{-14}	
Particulate-Form 2,3,7,8-TCDD (120 TPD)	1.1×10^{-13}	0.168	4.9×10^{-14}	0.028

2,3,7,8-TCDD on soil. This adsorption will occur when the vapor-phase plume reaches ground level and comes in contact with soil. For making an estimate, the soil phase concentration associated with the maximum air phase concentration was evaluated. Dispersion calculations showed that in all four scenarios the maximum deposition rate occurs at a distance (200 m) very close to the incinerator because of the building downdraft effects coupled with precipitation washdown. Since soil ingestion by children, and farming with a pond or stream in an area very close to the incinerator or at proximity of buildings within 200 m is considered unlikely, exposure from soil ingestion is evaluated at the site of the hypothetical family at 0.8 km from the stack. The difference in deposition rate between the maximum deposition rate and the rate at 0.8 km from the stack is approximately a factor of 6 as shown in Table 2.

SURFACE WATER CONTAMINATION

Two cases were evaluated for the extent of contamination of surface water by the emissions from the incinerator. In the first case, used in scenarios 1 and 2, a one acre pond, seven meters deep, was considered with a negligible amount of inflow and outflow water compared to the amount of water in the pond. In the second case, used in scenarios 3 and 4, the impact on a 300 meter wide, five meter deep river flowing at the rate of 0.5 m/s was considered. Both water bodies were located at 0.8 km from the incinerator.

The 2,3,7,8-TCDD emissions that reach the water bodies upon dispersion in the atmosphere will be composed of particulates and vapors. The characteristics of stack emissions are assumed to remain unchanged when the

emissions reach the water body, so that the ambient air concentrations above the surface of the water bodies are as shown in Table 2. These concentrations assume no photodegradation in the atmosphere in the process of pollutant transport from the stacks to the surface of water bodies.

Once the emissions from the incinerator reach water bodies nearby, the process responsible for transferring 2,3,7,8-TCDD in the atmosphere into the water are dry deposition, wet deposition and vapor absorption. The first two processes are responsible for the removal of particulates, and the last process removes the vapor-form 2,3,7,8-TCDD from the atmosphere. Dry deposition rates, which are outputs of air dispersion modeling, are used to estimate the concentration of 2,3,7,8-TCDD in the water body caused by the dry deposition. The two-resistance mass transfer theory was used to estimate the concentration of 2,3,7,8-TCDD in the water body caused by the absorption of vapors into water.

INCINERATOR EXPOSURE PATHWAY CALCULATIONS

Table 3 is a summary of the estimated environmental concentrations for the various incinerator scenarios, broken out by exposure pathway. It is to be noted that the concentrations in soil and food chain substances are given in mg/kg. The concentration in air and water are given in μg/m³ and μg/L, respectively. From these environmental concentrations, one can determine potential exposures corresponding to patterns of activities that one is likely to perform in one's daily life. Exposures represent daily intakes of 2,3,7,8-TCDD by humans from each pathway given, averaged over an individual's lifetime and divided by average human body weight. Exposure from all the pathways can occur over one's entire lifetime—as long as the population under consideration lives at the affected location. While the soil ingestion pathway is commonly assumed to occur during childhood only, the U.S. Environmental Protection Agency recently issued a policy statement providing an estimated soil ingestion rate for adults to be used in a risk assessment.

LAND DISPOSED ASH

The incinerator generates both bottom and fly ash which can be ultimately land-disposed. The disposal of bottom ash is not considered in this paper as noted previously. In some incinerator facilities, however, the fly ash and bottom ash are often mixed before disposal. If bottom ash has negligible amounts of 2,3,7,8-TCDD in it, this would result in a dilution of the concentration of 2,3,7,8-TCDD, thus reducing the concentration of 2,3,7,8-TCDD in fly ash mass being disposed of. The amount of

TABLE 3. ENVIRONMENTAL CONCENTRATION (MG/KG) ASSOCIATED WITH STACK EMISSIONS

Scenario	Vapor Form in Air ^a	Particu. Form in Air ^a	Soil	Water ^b	Beef	Fish ^c	Dairy
1 (3000TPD)	1×10^{-9}	6.5×10^{-10}	5.4×10^{-7}	1.6×10^{-9}	2.2×10^{-7}	1.6×10^{-8}	2.2×10^{-8}
2 (120TPD)	8.3×10^{-8}	5×10^{-8}	2.4×10^{-5}	1.3×10^{-7}	1×10^{-5}	1.3×10^{-6}	1×10^{-6}
3 (3000TPD)	1×10^{-9}	6.5×10^{-10}	5.4×10^{-7}	1.6×10^{-13}	2.2×10^{-7}	1.6×10^{-12}	2.2×10^{-8}
4 (120TPD)	8.3×10^{-8}	5×10^{-8}	2.4×10^{-5}	1.4×10^{-11}	1×10^{-5}	1.4×10^{-10}	1×10^{-6}

^a Units in μg/m³ at 0.8 km from incinerator.

^b Units in μg/L.

^c At bioconcentration factor of 10,000 L/kg.

TABLE 4. ENVIRONMENTAL CONCENTRATIONS (MG/KG) ASSOCIATED WITH FLY ASH DISPOSAL

Scenario	Vapor Form in Air ^a	Particu. Form in Air ^a	Soil	Water ^b	Beef	Fish ^c	Dairy
1 (3000TPD)	2×10^{-8}	7.6×10^{-10}	1×10^{-3}	8.4×10^{-7}	4×10^{-4}	8.4×10^{-6}	4×10^{-5}
2 (120TPD)	1×10^{-8}	3.7×10^{-10}	1.6×10^{-4}	1.4×10^{-7}	6.4×10^{-5}	1.4×10^{-6}	6.4×10^{-6}
3 (3000TPD)	2×10^{-8}	5.3×10^{-10}	1.4×10^{-6}	9×10^{-9}	5.2×10^{-7}	9×10^{-8}	5.2×10^{-8}
4 (120TPD)	6×10^{-9}	1.4×10^{-10}	1.3×10^{-6}	9×10^{-9}	5.2×10^{-7}	9×10^{-8}	5.2×10^{-8}

^a Units in $\mu\text{g}/\text{m}^3$ at 0.8 km from incinerator.

^b Units in $\mu\text{g}/\text{L}$.

^c At bioconcentration factor of 10,000 L/kg.

fly ash generated for land disposal can be estimated as follows: The uncontrolled emission factor for emissions of particulate matter from a municipal waste incinerator is 30 lb/T, as given in U.S. EPA, 1985 [12]. At a particulate emission control efficiency of 99%, the emission factor after control is 0.3 lb/T. For a 300 TPD capacity incinerator, the daily amount of fly ash collected for disposal is 3000 TPD \times (30-0.3) lb/T = 89, 100 lb per day. For the 120 TPD capacity, the amount of fly ash collected is 3,564 pounds per day.

The concentration of 2,3,7,8-TCDD in fly ash reported in the available literature varies from 0.07-100 ng/g (see Table 3). These data were mostly taken from municipal incinerators in European countries. The cause of the variation cannot be identified based on the data in the literature. Except for a Swedish study [1], the available literature data suggest that the concentration range of 2,3,7,8-TCDD in fly ash is 0.07 to 5.2 ng/g. An average value of 1.3 ng/g—excluding the Swedish study—was used for this study.

Receptors are assumed to be located off-site in fly ash disposal scenarios with distances at 100 feet and 500 feet for scenarios 1 and 2, and scenarios 3 and 4, respectively. The receptor areas are assumed to be about 10 acres for the purpose of estimating the soil concentrations.

Once fly ash is land-disposed, human exposure pathways similar to those for contaminated soil would result. Routes of exposure corresponding to these exposure pathways are shown in Table 4, along with the estimated environmental concentrations corresponding to each route of exposure. In all land disposal cases, it is assumed that no cover is applied over the disposed fly ash. Agricultural farms located in the vicinity of the landfill are assumed to estimate the concentrations in dairy products and beef. Fish contamination results from fly ash runoff which in turn will result in contamination of water and sediments. Air-borne particulates are formed as a result of wind erosion. Although the vapor pressure for 2,3,7,8-TCDD is

extremely low, volatilization could still occur at the rate corresponding to its vapor or partial pressure. It is believed that moisture in the soil pores due to precipitation could enhance the rate of volatilization.

EQUIVALENT TOXICITY FACTOR FOR TOTAL CDDs VERSUS 2,3,7,8-TCDD

Toxicity information is needed to conduct the risk assessment analysis using the estimated environmental concentrations. Stack emissions and fly ash contain many types of CDD congeners. Each congener can exhibit different toxic effects. In an effort to deal with the problem of different levels of toxicity for different congeners, U.S. EPA [13] developed the equivalent toxicity factors for other dioxins in relation to the most toxic 2,3,7,8-TCDD. The term Equivalency Factor (EF) is used to refer to the amount of 2,3,7,8-TCDD which would have the same toxicity as a CDD mixture. If the mass fractions of all congeners in stack emissions or fly ash containing a mixture of CDDs are known, these emissions or ash can be converted to the mass of 2,3,7,8-TCDD with equivalent toxicity.

All available literature data with information on the concentration of 2,3,7,8-TCDD in the samples taken were analyzed to obtain the adjusted weight percent for the total dioxin components. Appropriate data on emissions were obtained from 13 different incinerators and appropriate data on fly ash were obtained from six different incinerators.

Table 5 illustrates the calculations performed to derive the equivalency toxicity factor based on the analysis of congeners in stack emissions. Similar analyses can be performed for the congeners in fly ash. The weight fraction of each congener was averaged from the available data. The weight fractions calculated were multiplied by the EF shown on the table to obtain the adjusted weight percent.

TABLE 5. TOXICITY EQUIVALENTS OF CDD CONGENERS IN MWI STACK EMISSIONS

Congener	Emission Factors ($\mu\text{g}/\text{kg}$)	Percent	EF	Weighted EF (Percent \times EF)	Toxicity Equivalent
2,3,7,8	0.404	0.45	1	0.45	2.7
Other tetras	7.79	8.7	0.01	0.087	0.53
Pentas	25.87	29.07	0.5	14.5	88.2
Hexas	30.76	34.56	0.04	1.38	8.4
Heptas	16.85	18.93	0.001	0.019	0.12
Octas	7.32	8.22	0	0	
Total	89	99.98		16.44	99.95

Table 5 shows that for stack emissions, the total CDD constituents could be more toxic than 2,3,7,8-TCDD by a factor of $100/2.7 = 37$. This indicates that toxic effects associated with the releases of the total dioxin constituents in the stack would be higher than those from exposure to 2,3,7,8-TCDD by a factor of about 37.

These ratios represent averages derived from numerous incinerators. However, the ratio applicable to any one incinerator appears to vary widely. For example, a municipal waste incinerator in Marion County, Oklahoma was reported to have an adjusted weight percent of 2,3,7,8-TCDD of 85%-92% [9]. These data would suggest that the total CDD constituents are more toxic than 2,3,7,8-TCDD by a factor of only 1.1.

A similar analysis was conducted on available fly ash data (not listed here). This analysis indicates that the adjusted weight percent of 2,3,7,8-TCDD in fly ash is about 6.5%. This suggests that the total CDD constituents are more toxic than 2,3,7,8-TCDD by a factor of about 15.

The above procedure using TCDD equivalents to estimate total TCDD toxicity involves considerable uncertainty. The procedure assumes that the fate and transport properties of the CDD congeners are identical with those of 2,3,7,8-TCDD. Since the chemical and physical properties are not identical for each constituent of dioxins in stack emissions or fly ash, the environmental partitioning, degradation rates, and human absorption are likely to be different.

UNCERTAINTY ASSESSMENT

The incinerator scenarios address two model incinerators: an incinerator of moderate size assumed to have a high dioxin emission factor and a large incinerator assumed to have a low emission factor. The second incinerator model is intended to represent control which is more efficient than the first. The incineration scenarios are used to estimate environmental concentrations resulting from incinerator stack emissions and landfilled fly ash.

The land disposal scenarios address several simplified situations. These scenarios vary by the degree to which the contaminated material is maintained and controlled, the distance to human residences, and the presence of water bodies and agriculture. These physical scenarios are intended to represent occurrences that will be commonly encountered in the field, whether it is a reasonable worst case or typical situation. In these scenarios a constant concentration of 2,3,7,8-TCDD is assumed across the contaminated site. In the absence of detailed site-specific information, use of an average site concentration to calculate off-site environmental concentrations is deemed a useful procedure.

These scenarios are intended to illustrate a range of circumstances that may be encountered, rather than predict concentrations that will occur at specific sites. It may be expected that some factors affecting emissions will vary markedly between sites. As such, it is not meaningful to discuss the uncertainty present in the simplified physical

scenarios. More importantly, the methods used in assessing these scenarios can be applied to a variety of other physical situations that may be encountered.

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An Overview of Solvent Extraction Treatment Technologies

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In the course of evaluating potential technologies for treatment of contaminated soils at a regulated site in the upper Midwest, solvent extraction technology was reviewed and appeared to be a viable alternative to incineration and land disposal. Because of stringent federal and state land disposal rules, liability issues, and rising disposal costs, technologies that will treat and detoxify hazardous wastes effectively are preferred over other less aggressive technologies. Industry is actively seeking and evaluating options, and the regulatory community is encouraging development and application of new treatment technologies as alternatives to land disposal. To advance this effort, the U.S. Environmental Protection Agency (EPA) established the Superfund Innovative Technology Evaluation (SITE) program to promote the development of innovative technologies and to demonstrate such technologies at Superfund sites. Solvent extraction technology is being evaluated in the SITE program. This paper was prepared because of the lack of a compiled source of existing information on the alternative use of solvent extraction technology for treating soils contaminated with hazardous substances in a manner other than incineration.

INTRODUCTION

The solvent extraction technology has not yet been fully developed for hazardous waste treatment applications. Many solvent extraction systems are in the late development stage, very near full-scale commercialization. The market remains wary, waiting until the technology is fully developed and demonstrated before it is readily employed by industry. Because of regulatory requirements, some industries such as petroleum refining, where solvent extraction is considered a Best Demonstrated Available Technology (BDAT) for refinery wastes, are just beginning to apply the technology to address their waste management problems.

This overview of solvent extraction technologies was compiled from material collected in preparation for a solvent extraction bench-scale test for a hazardous waste

site in the Midwest. The information herein was obtained from process developers.

BACKGROUND

Solvent extraction has a long history of use. The food industry uses solvent extraction to extract vegetable oils, to decaffeinate coffee, and to remove the bitter taste from hops. The tobacco industry uses it to remove tar and nicotine from tobacco. Pharmaceutical manufacturers recover valuable products from plant roots, leaves, and stems. Solvent extraction processes have been especially important in nuclear reprocessing industries to separate and purify nuclear materials. The metallurgical industry commonly applies solvent leaching operations to retrieve valuable minerals from ores. Solvent extraction processes

are also used for resource recovery from manufacturing wastewaters, removal of noxious and hazardous materials from coal processing operations, reduction of the organic material in sewage, and de-oiling quench waters in refinery processing operations. The basic solvent extraction technology is over a hundred years old, but the applications of the technology are new. It is now being used to treat sediments and soils with polychlorinated biphenyls (PCBs), contaminated oily refinery wastes, wastes generated by chemical manufacturers, and hazardous and toxic wastes.

Several solvent extraction systems have been proposed as viable technologies for decontaminating oily hazardous waste materials—wastes that are typically expensive and difficult to treat. These wastes have usually been incinerated, landfarmed, or disposed of on land. Conceptually, application of a solvent extraction process might isolate organic contaminants in a form more amenable to treatment, recover oil for recycling, reduce contaminant levels in the solid phase below action levels, and reduce disposal volumes and costs. Solvent extraction has several advantages over thermal treatment. Some benefits arise because it is a recovery process rather than a destructive process, and solvent extraction can often recover valuable products and reclaim some soils. Solvent extraction may be easier to permit (since it is not subject to the same regulatory structures as incineration), may be economically feasible for treating a wider range of hazardous wastes, and can be considerably less costly with respect to energy requirements.

The successful application of solvent extraction depends on solvent selection, process configuration, specific contaminants and their concentrations, the waste source, the economic value of potentially recoverable compounds, and the overall economics of the process. Thus, solvent extraction should be considered if (1) the process is capable of yielding uncontaminated residual materials; (2) it is available on a commercial scale and has been successfully operated over an extended period; (3) valuable products can be recovered; (4) it is more economical than other treatment technologies; (5) the selected solvent is readily available at minimal cost; (6) any process solvent residue in the product streams is nonhazardous; and (7) inordinate wastewater disposal or air emissions problems are not encountered.

TECHNOLOGY REVIEW

Several innovative solvent extraction systems have recently become available for treatment of hazardous wastes. The following is an overview of some of the solvent extraction systems being introduced and applied to treat hazardous materials as well as those still in the developmental stage. The overview is not technically rigorous and is primarily based on information supplied by the developers.

CF SYSTEMS EXTRACTION PROCESS

Development

CF Systems Corporation has developed a solvent extraction process that uses critical fluids and liquefied gases such as carbon dioxide, propane, or other light hydrocarbons at high pressure to separate and recover oils from refinery sludges and to extract hazardous organic compounds from wastewater, sludge, sediment, and soil. The process typically uses propane on contaminated soil and sludge and carbon dioxide to treat wastewater. These solvents provide high extraction efficiencies, evaporate readily from extracted organic material, and have high

solubilities for most organic priority pollutants. They are inexpensive, readily available, nontoxic, and easily separated and retrieved from the process products.

The CF Systems process has extracted and separated organic constituents from treated manufacturing process wastewaters and refinery sludges and soils, and decontaminated wastes from wood treatment operations and industrial waste dumps.

PROCESS DESCRIPTION

The extraction process consists of four basic unit operations: solvent extraction, phase separation, solvent recovery, and filtration (Figure 1). Prior to processing, the particle size of the feed material must be reduced, typically to at least 5 mm diameter, and the feedstock must be pumpable. To process hazardous soil or sludge, the waste is slurried and fed into the top of the extractor. The solvent (propane), condensed by compression, flows upward through the extractor. The condensed solvent contacts the waste slurry, rapidly dissolves the oils, and extracts most of the organic contaminants from the water. When extraction is complete, the clean water/solids mixture is withdrawn from the bottom of the extractor. The contaminated solvent is discharged from the top of the extractor and passed through a pressure reduction valve to a separator. In the separator, the extraction solvent is vaporized, recompressed, and recycled to the process as fresh solvent. The extracted organic contaminants are recovered from the separator for treatment in a separate process. Several stages of extraction and decanting may be required to attain a given cleanup level. Reportedly, up to 90 percent of the solvent is recycled in the system; the remaining 10 percent retains the extracted contaminants.

Applications

The CF Systems process was demonstrated at pilot-scale for the U.S. EPA's SITE program and shown to be capable of removing PCBs from contaminated harbor sediments. More recently, CF Systems installed a commercial 300-barrel-per-day system to remove organic contaminants and reduce the oil and grease content of refinery sludges from the Star Enterprise Refinery in Port Arthur, Texas. This is the first reported commercial installation of a liquefied gas solvent extraction process to treat waste.

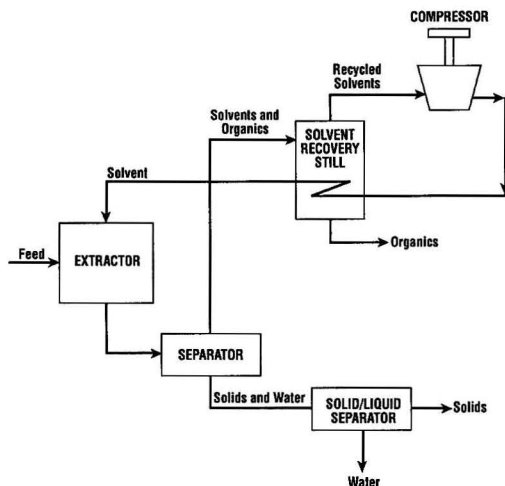


Figure 1. Simplified process flow of CF Systems extraction process.

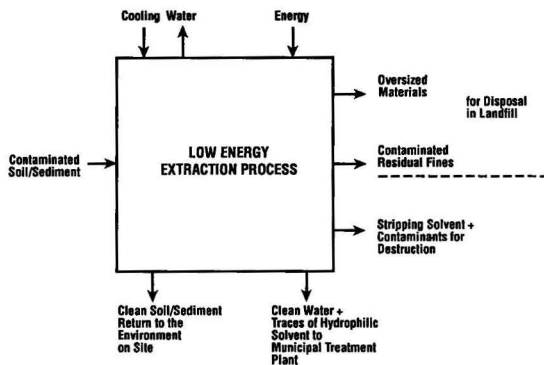


Figure 2. Streams entering and exiting LEEP.

Availability

CF Systems' skid-mounted mobile treatment unit has a 350-barrel-per-day capacity for on-site treatment. It has been used to treat refinery wastes, impoundment wastes, and other contaminated soils, sediments, and sludges. However, the pilot plant does not include all the ancillary subsystems that may be required for full-scale applications. A trailer-mounted demonstration unit capable of processing up to 20 barrels per day of feedstock is also available. This unit has operated at a number of refineries and chemical manufacturing plants.

Summary

The CF Systems extraction process is reportedly capable of treating oily wastes having any ratio of oil, solids, or water and can extract up to 99 percent of liquid hydrocarbons from waste. Favorable process features may include low operation costs, use of an inexpensive recoverable solvent, and operation at ambient temperatures. The most notable disadvantage of the process is related to materials handling. Since the waste must be slurried before processing, the process may not be applicable to wastes with too broad a range of particle sizes. If larger particles are screened out prior to processing, disposal of the untreated reject material may add to process costs. Also, the process equipment may be costly because of the high operating pressures required and the design safety features needed when using a flammable solvent. In addition, uncontrolled solvent losses raise safety concerns, and controlled solvent release by flaring may require a permit.

LOW ENERGY EXTRACTION PROCESS (LEEP)

Development

The Low Energy Extraction Process (LEEP) was developed by a New York University research team to provide a cost-effective process for removing PCBs from soil, sediment, and sludge. It is the result of a study funded by the U.S. EPA to develop and evaluate a low energy technology that would extract PCBs and other organic contaminants and concentrate them in the extract for subsequent chemical destruction. The process was originally designed to remove PCBs and organic compounds from hazardous waste materials.

The patented LEEP technology is being refined and commercialized by Remediation Technology, Inc. (REMTECH). The process extracts hydrophobic (water immiscible) organic compounds, including most of the priority pollutants from contaminated soil, sediment, and

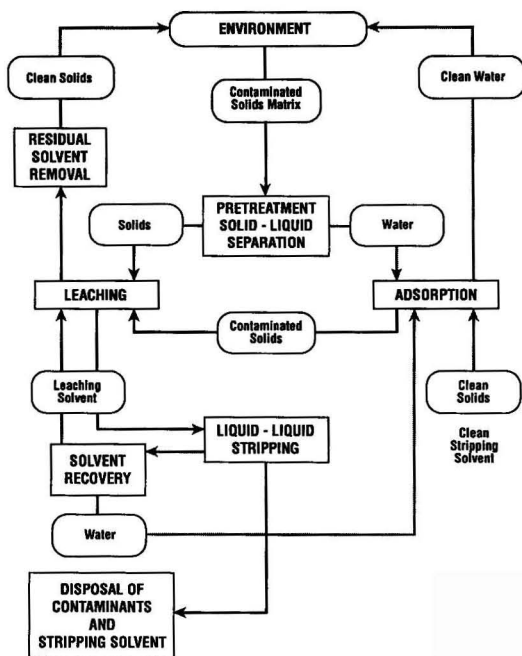


Figure 3. LEEP process flow.

sludge by using common hydrophilic (water miscible) and hydrophobic organic solvents. Acetone was selected as the hydrophilic leaching solvent and kerosene as the hydrophobic stripping solvent.

The process has been applied to PCB-contaminated soils and sediments, oily refinery sludges, and waste filter cake from a slop oil recovery process.

Process Description

The LEEP technology comprises six basic unit operations: solid-liquid separation, solvent extraction, distillation, adsorption, air stripping, and liquid-liquid extraction.

The process separates contaminated soil, sediment, or sludge into its liquid and solid fractions; extracts the organic contaminants in the solid fraction with a hydrophilic leaching solvent; transfers and concentrates the leached organic contaminants to a hydrophobic stripping solvent; and removes the contaminants from the process for destructive treatment. Process feed material must be screened to less than 1/2 inch in diameter prior to extraction.

Contaminants are removed from the separated water by adsorption onto a small portion of the cleaned solids or an alternate medium if necessary. All solvents are recycled to the system (Figure 2 and 3). Oversized material is washed with water and stored for disposal.

The first step in the process is a simple physical separation of water and solids by filtration or centrifugation using commercially available equipment. Typically, up to 40 percent of the water is separated from the solids in the first step.

Organic contaminants are then leached from the product solids with acetone in a multi-stage extraction process. The leaching process is performed in a counter-current paddle washer that discharges two process streams: an acetone/water mixture containing most of the organic

contaminant, and a slurry of uncontaminated soil and acetone. Solvent is recovered from the soil/acetone slurry by steam stripping and is recycled to the process. The cleaned solids are returned to the environment.

In the third step, the concentrated acetone/water mixture is contacted with kerosene and potassium sulfate (K_2SO_4) in a countercurrent centrifugal liquid-liquid extractor. The K_2SO_4 drives the organic contaminants out of the acetone and concentrates them in the kerosene, which is a nonpolar hydrophobic stripping solvent that is more amenable to chemical destruction than water. The extractor discharges two product streams: the contaminated kerosene, which is concentrated and then destroyed, and the acetone/water mixture, which contains trace concentrations of the organic contaminants. The acetone is recovered from the acetone/water stream by distillation and recycled to the process; the contaminated water is returned to the liquid-liquid extraction feedstream.

The water from the initial solid-water separation process in Step 1 is sent to an adsorption unit that contains a small portion of the cleaned soil obtained from the extraction performed in Step 2. The cleaned soil adsorbs some of the organic contaminants as the water passes through the adsorption unit. In a low solids feedstream, an alternative adsorption media is employed. In each case, two product streams exit the adsorption unit: the contaminated adsorption medium (soil) and the decontaminated water. The contaminated soil is combined with the raw waste stream entering the leaching unit in Step 2, and the treated water is discharged to the environment after suitable treatment.

Finally, the solvent is recovered from the soil/solvent product stream (Step 2) by steam stripping and recycled to the process. The cleaned solids are returned to the environment.

Application

LEEP was successfully applied at bench-scale to treat PCB-contaminated sediment from the Waukegan Harbor in Illinois. REMTECH recently completed bench-scale studies using the LEEP technology to treat refinery sludges at two refineries. For both sludges, the LEEP technology significantly reduced the volatile and semivolatile priority pollutant concentrations to levels below detection limits. In a recent evaluation of alternative technologies conducted by the Research Triangle Institute (RTI) under a U.S. EPA contract for the treatment of PCB-contaminated sediments, the RTI rated the LEEP technology one of the most economical of those processes evaluated.

REMTECH has recently developed a process that is combined with the LEEP technology to remove both organic contaminants and metals from contaminated soil, sediment, or sludge. The combined process has been applied to a refinery sludge and reportedly produced organic-free solids and reduced the metals concentration significantly. Process details are unavailable at this time. The U.S. EPA has selected REMTECH to demonstrate a pilot-scale system of the combined LEEP technology in the SITE program.

Availability

The LEEP technology is currently available for bench-scale treatability studies. A skid-mounted, pilot-scale unit is being constructed and will be available for treatability studies within 6 months and for field demonstrations within a year. It will combine the metals treating process with the LEEP technology.

Summary

The LEEP technology combined with the metals removal process could provide a versatile system capable of treating a mixed stream of organic contaminants and metals. The system is being pilot tested and will not be commercially available until at least 1990. The LEEP technology provides some desirable features. Because the system uses basic unit operations and is constructed with commercially available equipment, it is not bound by specialized process equipment and each unit operation can be replaced with a different commercial unit that might be more suitable for a specific waste stream. Major disadvantages are that the system is not yet available for full-scale applications and that feedstream particle size requirements may limit process applications. More development and demonstration at a larger scale are needed before LEEP can be considered for site remediation.

BP OIL SOLVENT EXTRACTION PROCESS

Development

To comply with the 1984 RCRA land ban amendments regulating the management of oily refinery wastes, BP Oil independently evaluated potential treatment technologies that would meet the U.S. EPA's BDAT for refinery wastes. A bench-scale solvent extraction system developed by Standard Oil was among the technologies evaluated, and it proved to be one of the more feasible treatment alternatives. It had the potential for meeting the BDAT limits and was capable of converting the oily refinery waste to a delistable (nonhazardous) material.

BP Oil decided to develop the Standard Oil solvent extraction process and advanced it to pilot-scale. A pilot plant successfully processed sludges from two Standard Oil refineries. A full-scale demonstration plant was then tested at the Alliance Refinery in Belle Chase, Louisiana. With the test results from the full-scale demonstration, BP Oil proposed solvent extraction as a BDAT for refinery wastes. In regulations promulgated on August 17, 1988, the U.S. EPA selected solvent extraction along with incineration as the BDAT for pretreatment of oily refinery wastes.

Process Description

The BP solvent extraction process consists of three unit operations: deliquification (filtration with additives), solvent extraction, and chemical fixation (Figure 4). Deliquification is a mechanical process used to separate water and oil from the refinery sludge. Sludge material is mixed with a filtration aid (0.5 to 1 part filtration aid per 1 part dry solids) and then routed to a recessed plate filter press operating at 100 psig pressure and temperatures of 100°F to 150°F. Two product streams are generated. The pressed solids are sent to the extraction unit and the oil/

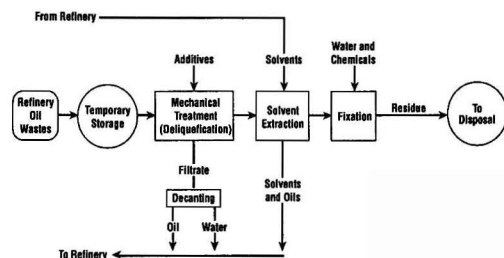


Figure 4. BP Oil solvent extraction system refinery waste treatment by solvent extraction.

water stream is separated. The recovered oil is returned to the refinery process and the water is sent elsewhere for treatment.

The pressed solids are directed to a specialized batch extraction vessel where they are contacted with hydrocarbon extraction solvents. Extraction is performed as a single or multiple cycle process, depending on the nature of the feedstream and the treatment goals. The single cycle operation performs a solvent wash of the sludge that is capable of removing less toxic compounds like xylene and naphthalene. The multiple cycle process employs two solvents over three extraction cycles and effectively removes the heavier multi-ring polynuclear aromatic hydrocarbons. The spent solvents are recycled to the refinery process.

Two process streams result from the extraction step. The oil-free solids are slurried with water and removed from the reactor. The slurried sludge is dewatered in a conventional filter press along with fixation additives that induce pozzolanic reactions that immobilize metals and other inorganic constituents.

BP Oil reports that its solvent extraction system is capable of separating more than 98 percent of the oil from the raw sludge and reduces the raw sludge volume by approximately 75 percent. Refinery sludges treated in the multiple cycle process meet all the U.S. EPA limits for organic compounds. The fixation step immobilizes the inorganic constituents and renders them unleachable.

Applications

BP Oil recently converted its full-scale demonstration plant to an operational commercial-size plant. The process is incorporated as a part of the refinery process and is reportedly capable of converting 15 tons of dewatered sludge per day (equivalent to a 100,000 bpd refinery) into 7 tons of petroleum feedstock.

Availability

BP Oil has made its proprietary solvent extraction process commercially available to other refineries. The unit is incorporated into existing refinery operations as an automated sludge recycling unit. BP Oil is accepting samples from other refineries for testing, but specific process information is available only to its clients due to a secrecy agreement.

Summary

The BP Oil solvent extraction process was designed specifically for refinery wastes and is intended to be a part of the refinery process. The process is easily licensed, complies with BDAT limits, is a cost-competitive alternative to incineration, has no air emissions, and recovers product.

B.E.S.T.® PROCESS

Development

Resources Conservation Company's Basic Extractive Sludge Treatment (B.E.S.T.®) process technology was invented during the 1960s by Boeing Company to process wastes generated during the manned space flights. Since then, Resources Conservation Company (RCC) of Bellevue, Washington, owner of the B.E.S.T.® patents, has developed the B.E.S.T.® process from laboratory-scale testing through prototype full-scale operation. The process has been tested on municipal wastewater sludge, petro-

leum refinery wastes, PCB-contaminated soils and sediments, and oily hazardous wastes at regulated sites.

Process Description

The B.E.S.T.® process is configured to exploit the unique solvent properties of triethylamine (TEA). Triethylamine easily breaks the oil/water emulsions that cause major problems in some separation processes. At or below 20°C, TEA is completely miscible with water; when heated above that temperature, TEA and water are only partially miscible. This "inverse miscibility" property is used by letting the oil and water components of a waste combine with the TEA to form a homogeneous, single-phase extraction mixture of oil/water/TEA. When the oil/water emulsion is broken, bonded water is liberated and the bound particulates are released from the solution. The extraction efficiency of the system is enhanced because the amine solvent is able to achieve intimate contact with all components of the waste.

Before the extraction process is begun, feed material must be screened and pH adjusted to an alkaline condition. The feed is then introduced into a mixing tank and combined with TEA chilled to temperatures below the miscibility point (<20°C). At that temperature, a single liquid phase is formed and the solid material settles out. The mixture is agitated until equilibrium is reached, then the solids are removed from the solution either by filtration or centrifugation (Figure 5). Multiple extraction stages may be required to achieve contaminant removal target levels.

The liquid fraction, a single-phase oil/water/TEA mixture, is heated to a temperature of 20°C and two distinct phases form—an aqueous phase and an organic phase made up of oil and TEA. The phases are separated by decantation into an oil/TEA phase and heavier water phase. The oil/TEA phase contains virtually all the oily material and organic contaminants. The TEA is recovered from the oil/TEA fraction by flash evaporation and steam stripping. Residual TEA is removed from the water layer by steam stripping. Recovered TEA is chilled and recycled for use in the process system.

The separated solids are returned to the feed tank for additional extraction with TEA. When extraction has been completed, solids are centrifuged or filtered and then dried to remove residual TEA and water.

Oil, water, and solids are produced by the process. Ideally, the product water can be conveyed to a water treatment facility for minimal treatment and discharged to the environment. The oil fraction may be reused as fuel, recycled, or destroyed if the organic contaminant levels in the oil are too high. The solids fraction may be returned to the site or sent to a disposal facility. The

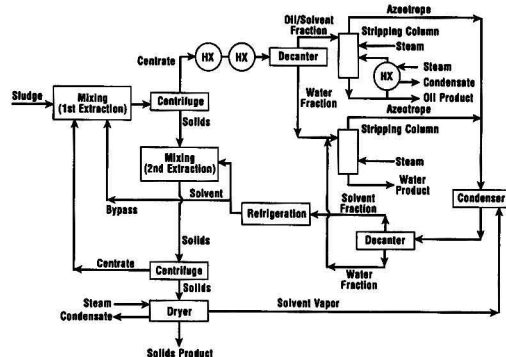


Figure 5. B.E.S.T.® process flow diagram.

B.E.S.T.[®] process operates at or near ambient temperatures and pressures and is completely enclosed to prevent air emissions.

APPLICATION

RCC has bench tested hazardous sludges from several oil refineries and fabricated a pilot test program for the American Petroleum Institute (API) to evaluate various technologies for treating refinery wastes to meet BDAT standards. RCC also participated in a study conducted by the Research Triangle Institute that evaluated alternative process technologies to decontaminate PCB-contaminated sediments. Of the eight treatment processes evaluated, the B.E.S.T.[®] process was rated one of the top three candidates selected for test and evaluation. The candidate processes were rated on their ability to reduce PCB concentrations to target levels, availability of a test system, process costs, and future commercial availability.

The U.S. EPA selected the B.E.S.T.[®] process for its SITE program. Process performance was evaluated near Savannah, Georgia, at the General Refining Superfund site, an abandoned waste oil refining facility that contained four acidic oily sludge ponds with high levels of heavy metals and detectable PCB concentrations. The average composition of the sludge from the four lagoons was 10 percent oil, 20 percent solids, and 70 percent water. RCC used its 100-ton-per-day, full-scale modular unit to process the sludge. The three product streams required minimal treatment. The product water was sent to a nearby industrial wastewater treatment plant and discharged. The product solids were retained at the site and encapsulated in the emptied lagoons. The recovered oil was recycled to an independent fuel blending operation.

AVAILABILITY

RCC performs a bench-scale glassware test at its Bellevue laboratory to simulate the process operation at full-scale. A small, mobile, truck-mounted extraction unit is available to process contaminated soil, sludge, or sediment at a rate of one cubic yard per hour. A 100-ton-per-day, skid-mounted commercial unit is available for on-site processing.

SUMMARY

The B.E.S.T.[®] process has been actively tested on refinery wastes and other oily hazardous wastes. RCC reports its system is capable of treating wastes with a broad range of oil, water, and solids composition and it has been effective in decontaminating refinery wastes. Reportedly, the process can achieve removal efficiencies that exceed 98 percent for organic compounds, but it has limitations. The pretreatment material sizing requirements could limit processing applications or add significantly to processing costs since oversized material would require some form of treatment. Also, since triethylamine is expensive, initial solvent costs could be high.

ACCUREX SOLVENT EXTRACTION PROCESS

Development

The Accurex solvent extraction process was procured by Envrite Field Services, Inc., and then by Harmon Environmental. The process was further developed, resulting in some process modifications and a new solvent blend. Specific information regarding these changes is unavailable. Therefore, the process referred to here is the original Accurex solvent extraction process.

The Accurex process was developed as a result of a 1983 research program sponsored by the Electric Power Research Institute (EPRI). EPRI sponsored the research in response to utility industry concerns about the cleanup and disposal of soils contaminated with PCBs. A series of laboratory, pilot-scale, and prototype full-scale tests were conducted to refine and develop a solvent extraction process that was technically and economically capable of reducing PCB levels in contaminated soils to less than 2 ppm. During the study, several polar and nonpolar solvents and solvent blends were tested, resulting in the development of a patented solvent blend consisting of fluorocarbon-113 (FC-113) combined with methanol.

Process Description

The original portable, full-scale Accurex solvent extraction system consists of a soil contactor, a modified ready-mix concrete truck, a spent solvent storage tank, and a 45-foot trailer containing solvent storage tanks, a solvent recovery system, storage vessels, and an electric steam boiler (Figure 6). To operate the system, the contactor is charged with contaminated soil and solvent is added. The contactor is rotated to mix the contents until equilibrium is reached, and then the solvent is drawn off. The contaminated solvent is transferred to a reclamation system where it is decanted into two layers. The water layer is discharged from the system. The contaminated solvent layer is distilled and the contaminants are concentrated as still bottoms. The contaminated still bottoms are removed for further treatment or destruction as required.

Typically, the soils are first washed at least twice with pure FC-113 to displace most of the water and reduce the PCB concentration. Then the methanol blend is added followed by a final addition of FC-113. When the target contaminant levels are reached, the washed soil is removed from the contactor and steam-stripped to remove the residual solvent. The cleaned soils can then be returned to the excavation or disposed of offsite.

Three product streams are produced. The liquid PCB-contaminated stream contains most of the organic contaminants, including oil and PCBs, and must undergo destructive treatment. The washed soil contains less than 2 ppm of PCBs and can be returned to the site as clean fill. The product water is the water that was present in the soil. Since PCBs exhibit low solubility in water and are usually present on suspended soil particles, simple filtering prior to discharge should render the water essentially PCB-free. Because the process is conducted at ambient temperatures, PCB emissions should not occur. Nonetheless, all vessels in the system are interconnected with a common vent system that leads to a noncontact

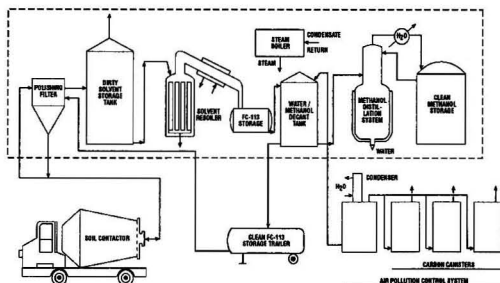


Figure 6. Accurex process prototype soil washing system.

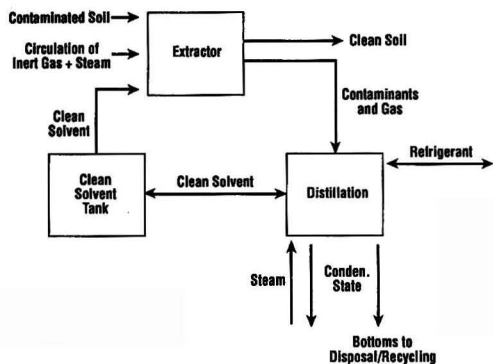


Figure 7. Extraksol™ solvent extraction process flow extraction mode.

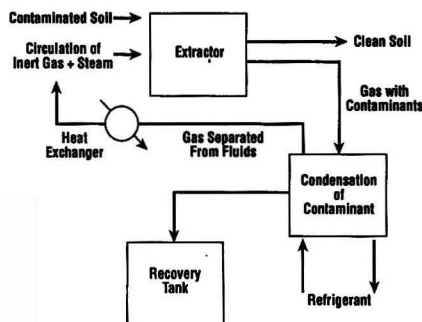


Figure 8. Extraksol™ solvent extraction process flow stripping mode.

condenser. The condenser removes residual solvents and is followed by a set of three activated carbon adsorbers as shown in Figure 6.

Applications

The Accurex solvent extraction process was selected to participate in the EPA's SITE program after it was procured by Envirote Field Services, Inc. Laboratory and pilot-scale studies are reportedly being conducted, but information is not available at this time.

Availability

Harmon Environmental reports the new, modified process will soon be available for full-scale treatment of oily refinery sludges and PCB-contaminated soils and sediments.

Summary

The Accurex process is not yet fully developed, but pilot-scale and prototype full-scale tests have demonstrated that the process is capable of significantly reducing PCB contaminant levels in soils. Preliminary cost analyses reported in the EPRI study indicate the process is competitive with landfill and incineration costs. The full-scale prototype study revealed problems related to the solvent contactor design and the materials handling. These are major problems because waste material must have good contact with the solvent to achieve acceptable extraction efficiencies and the desirable treatment levels. Harmon Environmental claims it has resolved this problem by redesigning the solvent contactor. It has also developed a solvent blend that is less objectionable environmentally.

EXTRAKSOL™ PROCESS

Development

The Extraksol™ process was developed in 1984 by Sanexen International, Inc., Ontario, to extract contaminants, particularly PCBs, from liquids, solids, and off rigid surfaces. The process was initially developed to extract nonvolatile contaminants and was used to decontaminate water, surfaces, transformers, debris, protective clothing, and miscellaneous equipment. In 1986, Sanexen developed and tested a pilot-scale mobile extraction system to treat contaminated soils. In 1987, a full-scale, 1-ton-per-hour demonstration unit was built

and operated. The success of the full-scale unit led to the construction of a 1.5-ton-per-hour commercial unit that is being used to treat PCB-contaminated soils and clays.

Process Description

A detailed process description was not readily available. The process is discussed in general detail as provided by the process developer. The Extraksol™ process extracts organic compounds from contaminated soils under a vacuum using a proprietary extraction fluid. The process design is based on the effectiveness of the proprietary solvent blend to remove particular target contaminants. After extraction, the spent solvent is distilled and recycled to the process, and the contaminants are either concentrated for final destruction or recovered. The process is operated in two modes. The extraction mode removes contaminants from the liquid phase (Figure 7), and the stripping mode removes contaminants from the gaseous phase (Figure 8). Feedstream pretreatment specifics were not provided, but should be assumed as a necessary part of any solvent extraction process.

Applications

Sanexen reports the Extraksol™ process has been used commercially in Canada to clean up spills and to remove PCBs and oils from contaminated soils and Fuller's earth (a hydrous clay used as an adsorbent in the refining and decolorizing of oils, as a catalyst, and as a bleaching agent). The process reportedly achieves 90 percent efficiencies for removal of PCBs, oil, and grease.

Availability

A mobile full-scale unit is available for spills, for site remediation work, or as a demonstration for larger-scale projects. The process is commercially available in Canada and may soon be marketed in the U.S. Sanexen also intends to construct a 6-ton-per-hour Extraksol™ unit.

Summary

The Extraksol™ process is similar to some of the commercially available processes and is available for full-scale application in Canada. The efficacy of the process for treating different hazardous waste streams cannot be evaluated here because the process has not been applied to any extent in the U.S. and the only limited information was provided by the developer.

TABLE 1. SUMMARY OF SOLVENT EXTRACTION TECHNOLOGIES

Firm	Process Name	Availability	Applications
CF Systems Corporation 140 Second Street Waltham, MA 02154-1100	CF Systems Extraction Process	Full-scale: 350 barrels per day on-site. Pilot-scale: 20 barrels per day.	PCB-contaminated soils and sediments. Refinery sludges. Industrial waste dumps. Wood treatment operations. Manufacturing process wastewaters.
REMTECH Remediation Technology Inc. 273 Franklin Road Randolph, NJ 07869	Low Energy Extraction Process (LEEP)	Bench-scale treatability studies. Pilot-scale under construction.	Mixed stream of organic contaminants and metals. PCB-contaminated soils and sediments. Refinery wastes.
BP Oil Company 200 Public Square 15-2206-C Cleveland, OH 44114-2375	BP Oil Solvent Extraction Process	Full-scale into refineries, specific process information for clients only.	Converting refinery sludge into petroleum feedstock.
Resources Conservation, Co. 3006 Northup Way Bellevue, WA 98004-1407	B.E.S.T.* Process	Bench-scale at RCC lab. Full-scale: 1 cubic yard per hour. Commercial-scale: 100 tons per day.	Refinery wastes. PCB-contaminated soils and sediments. Municipal wastewater sludge. Oily hazardous wastes.
Harmon Environmental 5221 Militia Road Plymouth Meeting, PA 19462	Accurex Solvent Extraction Process	Pilot-scale treatment in process. Full-scale under construction.	PCB-contaminated soils, sediments and refinery sludges.
Sanexen International, Inc. 3027 Harvester Rd., Unit 204 Burlington, Ontario L7N 3G7	Extraksol™ Process	Full-scale, mobile for on-site.	PCB- and oil-contaminated soils and sediments.

OVERALL SUMMARY

The six solvent extraction systems reviewed are summarized in Table 1. Each system has unique features that focus on achieving effective treatment of hazardous waste materials. All of the systems have been applied at the bench- and pilot-scale, and some are up to full-scale operation. Most of the applications have been on refinery wastes, PCB-contaminated wastes, and other oily hazardous wastes. The technology has many advantages as a waste treatment process and has been demonstrated to be effective on specific wastes. Site demonstrations continue as the technology evolves to accommodate the needs of the market.

Solvent extraction systems other than those mentioned may also be applicable for treating hazardous wastes. Though not addressed, European solvent washing systems have been used overseas for many years in hazardous waste cleanup applications.

Solvent extraction process technology still has some limitations. Some systems can handle a wide range of wastes with consistent treatment performance, whereas others are more susceptible to variable waste conditions. Because many of the processes tested thus far have processed wastes with little variability, treatability testing is necessary before they are implemented on a full-scale application. Additionally, caution in bench- and pilot-scale tests is warranted. Bench- and pilot-scale test results achieved by some processes may not be representative of the range of feedstock at full-scale conditions, so the results may not be reproducible.

The product waste streams of some systems may require treatment before disposal, and the spent solvents

may be toxic and also require treatment. In addition, wastewater treatment and disposal requirements may not be fully developed for some of the processes.

Solvent extraction systems have often been emphasized in bench and pilot testing, whereas integrated systems, including all ancillary subsystems, may still need to be demonstrated for control, subsystem interfacing, and versatility with variable feeds. Also, feed classification has generally been ignored in process descriptions and in cost estimates. Different solvents will be more or less effective for different organic contaminant types. Finally, many of the processes cannot effectively treat inorganic contaminants.

The solvent extraction process technology appears to be a viable alternative for treating some contaminated soils and sludges. As the technology continues to be applied more frequently to treat certain waste types, the various solvent extraction systems will be refined, and some of the process limitations summarized above may be minimized. It seems certain the technology will grow to meet the needs of the market.

ACKNOWLEDGMENT

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Use of an Air Inflated Dome to Control VOC Emissions from an Aeration Lagoon

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In 1979, the Upjohn Company entered into negotiations with the State of Connecticut for renewal of their NPDES permit. During these negotiations, control of odors from the site became an issue, and several methods of eliminating potential odor sources from the facility were examined. At this point in time, the waste treatment system consisted of a series of lagoons, the last one being an aeration lagoon with two 150 horsepower fixed aerators. One of the many potential odor sources to be addressed was this lagoon. As part of the permit renewal conditions, the State of Connecticut DEP ordered Upjohn to construct an air supported enclosure over the 9,500-11,350 m³ aeration lagoon. Exhaust air was to be monitored and treated with the use of fixed bed granular activated carbon absorbers. This resulted in a project costing over \$620,000 to construct and an additional \$75,000-\$100,000 per year to operate.

INTRODUCTION

While there are both positive and negative aspects to the operation of this type of device, it did provide a unique opportunity to study the disposition of regularly monitored organic compounds (benzene, toluene, ethylene dichloride, and chlorobenzene) that enter the treatment system. A complete mass balance of the system was performed by the Radian Corporation [1] in a report prepared for the EPA indicated the fate of various organic compounds (Tables 1 & 2). Samples of the influent, effluent, air space above the aeration lagoon, and wasted sludge

were used to determine the removal from the system of non-methane hydrocarbon compounds (NMHC) via biodegradation, waste water, sludge wasting, and air stripping. A table in the above mentioned report indicated an air stripping rate, referred to as Dome Exhaust, at 59% (see Table 1 & 2), with biodegradation accounting for only 19% of the destruction. It was believed that the biodegradation rate should have been higher since the average BOD removal from the system during the time of the study was 50%. In reviewing the data and calculations in the report, an error was found in the molecular weight of air used for the mass calculation which, when corrected, yielded a biodegradation rate of 60% and an air stripping

TABLE 1. FATE OF NMHCs UNDER AIR STRUCTURE: SUMMARY OF MASS BALANCE RESULTS
(Based on Averages of the Data)

Source of Effluent	NMHC Flow (Kg/min)	% of Influent
Influent		
Primary Clarifier Feed	0.212	100
Effluent		
Dome exhaust	0.125	59
Effluent wastewater	0.032	15
Effluent centrifuge sludge	0.014	7
Biological oxidation ^a	0.041	19

^a By difference

rate of 18%. While this gives much better correlation with the BOD removal, 50% to 60% is not a removal rate found in most well-operated activated sludge systems, municipal or industrial.

Radian conducted a study of removal efficiency around the carbon adsorber at the air outlet of the air structure. In a normal cycle, the carbon adsorber is in use for 24 hours, followed by an eight hour regeneration cycle using steam. The condensate from the steam regeneration is returned to the aeration lagoon. Results of this experiment showed virtually no removal of VOC compounds regardless of where in the cycle the study was performed. This is not as unusual as it may seem, when the conditions of operation of the adsorber are taken into account.

Air entering the adsorber is always at, or close to saturation. It is well known that wet carbon does not possess nearly the capacity of dry carbon to adsorb volatile organic compounds, consequently, pass through is not totally unexpected. However, this is not to say that the adsorber does not accomplish any useful purpose. While the study was conducted on VOC components of the stream, the dome was initially constructed to control odors emanating from the facility. Certain chlorinated phenols were identified as odor bodies in an earlier study. Odor threshold levels in the 4-20 ppb range were identified for these compounds which do not pass through the column unaffected.

TABLE 2. FATE OF NMHCs UNDER AIR STRUCTURE: SUMMARY OF MASS BALANCE RESULTS
(Based on Averages of the Data)

Source of Effluent	NMHC Flow (Kg/min)	Corrected % of Influent
Influent		
Primary Clarifier Feed	0.212	100
Effluent		
Dome exhaust	0.039	18
Effluent wastewater	0.032	15
Effluent centrifuge sludge	0.014	7
Biological oxidation ^a	0.127	60

^a By difference

At the time of the study, the bio-system was not optimized or at steady state conditions. Dredging of the lagoon bottom using floating aerators was being performed in an attempt to increase lagoon residence time. This stirred up load from the bottom of the lagoon and gave an extremely high F:M ratio. Wasting was occurring at an excessive rate to remove the large amounts of solids being dredged up from the lagoon. This had the effect of significantly lowering the mean cell residence time (MCRT) in the system. Under these conditions, it is not difficult to understand a BOD removal rate in the 50% to 60% range. After the initial study conducted by Radian, the lagoon operation was optimized and a new study undertaken by Upjohn was performed. This time the results were significantly different with biodegradation accounting for 99+% for benzene, toluene, and mono-chlorobenzene. A biodegradation rate of 80+% was achieved for 1,2 dichloroethane (ethylene dichloride), which is one of the more difficult to degrade organic compounds. It so happens that this component had the highest rate of volatilization in this study at a level of 1.95%. Therefore, it would appear that the control of the volatile organic components in this system is accomplished by biodegradation, rather than by capture under a dome and treatment with carbon (see Table 3).

This is not to say that this type of control technology does not have its place in the waste treatment field, but it

TABLE 3. FATE OF ORGANIC COMPOUNDS UNDER AIR STRUCTURE UPJOHN MASS BALANCE STUDY
(Average of Data)

Parameter	Influent kg	Effluent kg	Vent kg	Sludge kg	Percent BIO	Removal VOL	By ADSP
MC	0.017	0.016	0.000	0.004	6.73	0.00	1.29
EDC	5.081	0.876	0.098	0.008	80.64	1.95	0.04
Benzene	17.025	0.000	0.033	0.005	99.77	0.20	0.01
Toluene	5.257	0.000	0.004	0.005	99.83	0.07	0.01
MCB	3.052	0.016	0.003	0.005	99.18	0.11	0.06
OCP	5.098	0.000	0.000	0.008	99.84	0.00	0.16
Phenol	0.317	0.000	0.000	0.008	97.53	0.00	0.95
2,4-DCP	2.099	0.000	0.000	0.018	99.13	0.00	0.87
2,4,6-TCP	1.182	0.698	0.000	0.020	39.18	0.00	1.26
PCP	0.406	0.178	0.000	0.001	55.66	0.00	0.00
4-NP	4.780	0.292	0.000	0.300	87.60	0.00	6.29

MC = Methylene Chloride
EDC = 1,2 Dichloroethane
MCB = Monochlorobenzene
OCP = Orthochlorophenol
DCP = Dichlorophenol
TCP = Trichlorophenol
PCP = Pentachlorophenol
NP = Nitrophenol
BIO = Biological Destruction
VOL = Volatilization
ADSP = Adsorption

TABLE 4. EFFECT ON BIOLOGICAL DESTRUCTION MONTHLY CONVENTIONAL PARAMETER RESULTS
1987-1988

Month 1987	Pt. 3 BOD	Pt. 3 COD	Pt. 4 BOD	Pt. 4 COD	% Removal BOD	% Removal COD
January	531	1416	26	325	95.10%	77.05%
February	485	1997	26	236	94.64%	88.18%
March	719	1722	57	299	92.07%	82.64%
April	579	1444	54	276	90.67%	80.89%
May	552	1158	67	446	87.86%	61.49%
June	929	2357	162	834	82.56%	64.62%
July	237	613	65	356	72.57%	41.92%
August	575	1081	44	345	92.35%	68.09%
September	720	1650	45	408	93.75%	75.27%
October	883	1961	68	468	92.30%	76.13%
November	1073	2726	80	433	92.54%	84.12%
December	600	1814	76	450	87.33%	75.19%
1988						
January	496	1861	77	539	84.48%	71.04%
February	456	2176	22	267	95.18%	87.73%
March	855	2347	46	332	94.62%	85.85%
April	1070	2250	55	378	94.86%	83.20%
May	491	1850	24	317	95.11%	82.86%
June	546	2164	36	342	93.41%	84.20%
July	303	1661	20	276	93.40%	83.38%
August	399	1547	31	272	92.23%	82.42%
September	817	2945	33	236	95.96%	91.99%
October	513	1656	10	145	98.05%	91.24%
November	877	37063	25	201	97.15%	99.46%
December	323	834	10	171	96.90%	79.50%

should only be utilized where it can enhance the operation of the biological lagoon. Many operations in the northern parts of the United States have poor removals by biological means during the winter months. Low temperature effects on treatment efficiency are well documented, resulting in different limits being set by regulatory agencies for winter operation as opposed to the rest of the year. This device is extremely good at heat retention which facilitates higher removal efficiency during winter months. Unfortunately, like most positives, there is a negative side—which is the high temperature effects that take place in the summer months. Lagoon temperatures in the summer months in the Upjohn system are routinely in the 35°–40°C range and treatment efficiency drops to some degree (see Table 4). Areas south of Connecticut would probably routinely enter the thermophilic temperature range in biological lagoons, and the further south, the longer this phenomena would have to be controlled. To consider this technology in the south, engineering controls would have to be included in the system at the project inception, and would add significantly to the operational costs. Items such as influent coolers, air coolers, condensate return, and exhaust air heaters, with their inherent fouling and operational costs would have to be designed and included.

Temperature effects not only play a part in lagoon operation, but also in maintenance of equipment under the structure. Workers entering this environment must be fully protected using self-contained breathing apparatus or compressed breathing air. Impervious suits to protect skin from contamination are also highly desirable, as it is impossible to know every chemical constituent that may be present in the air under the structure.

Corrosion of equipment, removal for repair, and preventive maintenance are additional problems which must be addressed. The pH of the water vapor over the lagoon is that of carbonic acid at approximately 5.5. This acidic water vapor is being forced into the seals of every operating machine part at a pressure of 250 Pa. Methods must be devised to keep these corrosive vapors out of operating equipment.

Large pieces of equipment are virtually impossible to remove for repairs, unless large equipment airlock doors are provided in the initial design.

Maintenance items such as oil changes on fixed aerators require 4 to 8 times as much cost. As an example, the oil change on a 75 horsepower aerator previously required two men for four hours. This operation presently requires four men for eight hours.

Safety of the personnel working under the air supported structure is of prime concern. An entry to perform work under the structure requires four people. A compressor watch to assure air supply to the mechanics or operators, a shore watch, and two people working in a boat or on a barge. These people are required to be in sight and radio contact at all times. A special space entry permit has been designed to check not only oxygen content and explosive limit, but also air temperature. This is needed to prevent heat exhaustion from occurring to people working under the structure in the summer months, when the air temperature has reached levels of 40+°C. The amount of working time is limited as temperature increases above 18°C and entry is prohibited when 45°C is reached (see Figure 1). Excessive foam on the surface will also result in an entry being cancelled, as maneuverability is difficult and surfaces become slippery. Another internal environmental concern which will force cancellation of a work entry is noxious odors. While this only happens infrequently, anything detected in the air space that is above normal detection limits will cause a conservative attitude to be taken on the side of worker safety.

External environmental factors will also result in a structure entry being aborted. High winds and thunderstorms have the potential of damaging the structure and trapping people inside and this is an unacceptable risk.

Operational costs strictly related to the operation of the air structure basically consist of electricity to operate the inflation fan and vent fan. The cost of granular activated carbon for the adsorbers which is changed yearly must also be included. The operational costs are not unreasonable if added maintenance costs are not included.

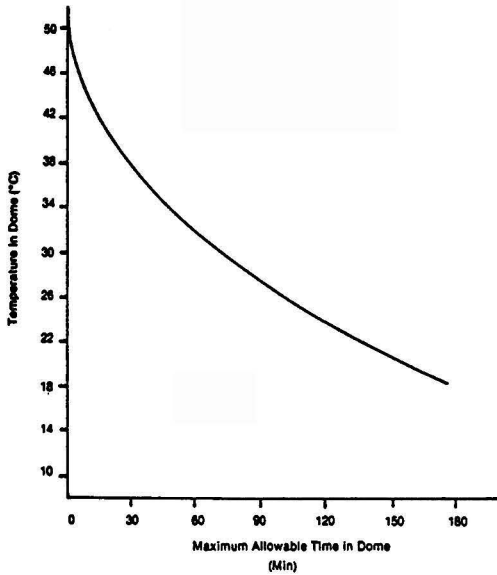


Figure 1. Maximum allowable time in dome for maintenance versus inside dome temperature.

If operation of the production plant is dependent on the waste treatment plant being enclosed, redundant systems must be provided. Normal systems would consist of an automatic back-up inflation fan should the main fan fail, and a propane fired fan should the electricity fail. While these cost nothing to operate in addition to the above costs, as normally only one inflation system is operating at a time, they do add to the initial capital cost and have to be maintained.

SUMMARY

Use of an air supported structure to control volatile organic emissions from an aeration lagoon is only effective insofar as the cover of the lagoon enhances biological degradation.

In warm climates, capital would be better invested in improving biological degradation than in covering aeration lagoons.

Maintenance costs for retrofit covers of this nature over aeration lagoons far exceed benefits of emission control.

Treatment of exhaust air from the structure with carbon can be efficient in removing noxious odors detectable at low levels.

LITERATURE CITED

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Startup and Operation of an Anaerobic Biological Activated Carbon (AnBAC) Process For Treatment of a High Strength Multicomponent Inhibitory Wastewater

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A joint study has been conducted by investigators at the State University of New York at Buffalo and Occidental Chemical Corporation to examine the feasibility of the anaerobic biological activated carbon (AnBAC) process for treatment of a high strength multicomponent inhibitory wastewater. The three principal components of the study waste are phenol, formaldehyde, and methanol. Bench-scale studies were conducted over a two-year period using 2.54 cm and 5.08 cm ID AnBAC columns. Based on the results of the bench-scale studies, organic contaminant removal of greater than 90 percent was achieved at loading rates of 0.06 g COD/g GAC/day. Subsequently, the results from the bench-scale studies were used to design a pilot-scale AnBAC system which has been operating successfully for approximately ten months at Occidental Chemical Corporation's Durez Division plant in North Tonawanda, New York. The purpose of this paper is to present performance data from both the bench- and pilot-scale systems and identify startup procedures found necessary for successful initiation of AnBAC column operation. Based on the data collected, the AnBAC process is capable of providing excellent treatment performance of the high strength waste. Proper balancing between the applied organic loading rate and the process removal capacity was found to be crucial in maintaining a healthy biomass during column startup due to the inhibitory nature of the wastewater.

INTRODUCTION

The Durez Division of Occidental Chemical Corporation located in North Tonawanda, New York manufactures phenolic resins. A thermoplastic resin, used in the manufacture of automobile and appliance parts requiring high temperature performance, is the principal product from the plant. The primary raw materials are phenol and formaldehyde, and these two compounds carry over into the strong liquor from the scrubber building. Currently the strong liquor is stripped of phenol and incinerated on-site. However, because the strong liquor is predom-

inately water, significant heat input is required for incineration. To find a more cost-effective treatment and disposal option for the strong liquor, Occidental Chemical Corporation began studies with the Department of Civil Engineering at the State University of New York at Buffalo in 1986. A sequenced anaerobic biological activated carbon (BAC)/aerobic BAC system was conceptualized as being an effective treatment process train and has been the focus of laboratory investigations. The purpose of this article is to present performance data related to operational characteristics of the anaerobic process employed for the study.

BACKGROUND

Anaerobic treatment of inhibitory wastewaters has received considerable attention during the past decade. The high rate of organic contaminant removal by biological assimilation witnessed in these studies demonstrates the feasibility of anaerobic treatment of inhibitory wastewaters (Khan, *et al.* [2], Kim, *et al.* [3], Suidan, *et al.* [5, 6, 7], Wang, *et al.* [8, 9]). Khan, *et al.* [2] pointed out the following advantages for anaerobic phenol treatment in a biological activated carbon reactor: low sludge production, ability to buffer transients due to adsorptive characteristic of GAC, and the process is more economical than conventional GAC treatment/regeneration for high strength wastewaters.

Unfortunately, comparison of the various studies on a common basis is difficult. Wang, *et al.* [9] expressed the organic loading as mass COD per external surface area of GAC per day. While this approach is sound, given the fundamental role that surface area plays in fixed film systems, the physical properties of the activated carbon external surfaces must be known. Although determinations of this type can be made by knowing the various size fractions and assuming the GAC particle to be spherical, this information is not reported often. Khan, *et al.* [2] used an organic loading rate based on reactor volume. However, volumetric loading rate as mass COD per unit volume per unit time is not applicable for fixed film systems because biomass levels are independent of reactor volume. Other researchers did not present organic loading rates on any basis, although the loading often could be derived with the given information.

To enable comparison between the results obtained by previous researchers and the results obtained in this study, the pertinent data available in the literature were transformed to an organic loading rate expressed as grams COD/gram GAC-day as shown in Table 1. The mass of GAC is the initial dry mass of activated carbon (103°C) and serves as a surrogate measure of the activated carbon surface area available for bacterial colonization.

Although this organic loading parameter is relatively simple to derive from the information presented in the literature, care must be taken when using it to compare between studies. For example, as the average diameter of the activated carbon decreases (US sieve size increases), the external surface area increases for a constant carbon mass. Thus different amounts of biomass would be expected even for the same mass of carbon. Carbon particle size also affects carbon bed expansion which in turn affects biomass levels as a result of shear stress and abrasion [4]. Fortunately, as noted in Table 1, the majority of applicable studies have been conducted using similar GAC particle sizes. Thus, comparison of the cited studies using the proposed organic loading rate expression is valid.

Based on a review of the maximum loadings studied by various researchers and the resulting soluble COD treatment efficiency as shown in Table 1, it may be concluded that AnBAC operating conditions presented in the literature reflect organic loading situations that are less than the maximum possible biological assimilation capacity.

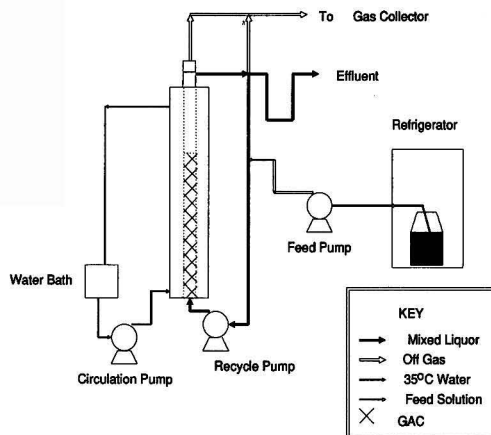


Figure 1. Process schematic for AnBAC systems employed during study.

Evidence for this conclusion is the consistently high contaminant removal at all levels of organic loading studied. Khan *et al.* [2] studied a maximum phenol loading of 0.015 g COD/g GAC-day and achieved COD removal efficiency between 87 and 93 percent. Wang, *et al.* [9] likewise loaded AnBAC columns with phenol at 0.019 g COD/g GAC-day and achieved 94 percent COD removal. Maximum loadings of toxic compounds that induce decreased methane production and lower treatment efficiency have not been reported.

MATERIALS AND METHODS

This study was conducted in three phases. Bench-scale studies employing four anaerobic BAC columns of 2.54 cm (1 inch) and 5.08 cm inside diameter (2 inch) were performed in Phases 1 and 2, respectively. Phase 3 was conducted under pilot-scale conditions by using two 17.8 cm (7 inch) inside diameter columns.

Column Construction and Operation

A schematic of the AnBAC system used throughout the three study phases is shown in Figure 1. Constructed of clear acrylic tubing, the columns were operated as upflow expanded beds. Recycle flowrates were set to provide a bed expansion of 25 to 40 percent of the initial non-expanded bed height which was dictated by such physical constraints as gas buildup in the bed and GAC bridging. A water jacket surrounded the column to maintain a constant 35°C operating temperature.

In Phase 1, four columns designated C1-C4, each filled with 100 grams of Calgon F-300 of sieve size 10 × 16 (C1, C3 and C4) or 16 × 20 (C2), were used for the investigations. Recycle and feed pumping was performed with peristaltic pumps. Operation of these columns was initiated in early 1987 at the University at Buffalo labora-

TABLE 1. SUMMARY OF MAXIMUM INHIBITORY LOADINGS USED IN ANBAC RESEARCH

Researcher	Primary Substrate	GAC Size Fraction	Loading Rate g COD/g GAC-day	Average COD Removal, %
Khan <i>et al.</i> [2]	Phenol	10 × 20	0.015	90
Wang <i>et al.</i> [9]	Phenol	16 × 20	0.019	94
Suidan <i>et al.</i> [5]	Catechol	10 × 20	0.012	95
Kim <i>et al.</i> [3]	Phenol	10 × 20	0.018	(1)

(1) Uncertain

TABLE 2. DESIGN FEATURES OF THE THREE ANBAC SYSTEMS

Parameter	Phase 1	Phase 2	Phase 3
	2.54 cm Bench Columns C1-C4	5.08 cm Bench Columns C1A-C4A	Pilot-Scale P1-P2
Column Diameter, cm	2.54	5.08	17.8
Initial Dry Mass of GAC, g	100	300	8500
Initial Bed Height, cm	43	38	76
Expanded Bed Height, cm	55	50	97
Empty Column Volume, L	0.9	2.2	30
Period of Operation, days	500-565	140-270	300 ⁽¹⁾

⁽¹⁾ Columns P1 and P2 continue to operate.

tories. Process startup was achieved through periodic column inoculation with an anaerobic population obtained from a western New York POTW. A 1,000 mg/L influent COD feed solution was used during startup for all columns. The startup period lasted for approximately three months.

Operation of the Phase 1 studies was conducted for over 500 days under varying organic and hydraulic retention times. Column reliability was a problem throughout the study because the recycle pump tubing was short lived and leaks developed which resulted in exposure of the anaerobic bioparticles to the atmosphere.

To overcome the recurring operational problems associated with the 2.54 cm Phase 1 columns, 5.08 cm columns designated as C1A-C4A were constructed and placed in operation in October of 1988. The columns contained 300 grams of Calgon F-300 activated carbon. To seed the columns, the GAC from the four Phase 1 columns was sampled, then combined, mixed, and split into four equal portions of approximately 82 grams. The 82 grams of viable biomass-coated GAC were then supplemented with 218 grams of virgin Calgon F-300 activated carbon of 8 x 16 sieve size, bringing the total GAC to 300 grams in each of the columns. Recycle pumps for the 5.08 cm columns were magnetic drive centrifugal pumps that provided relatively maintenance free operation. The feed was pumped with peristaltic pumps. Operation of columns C1A-C3A was discontinued in May 1989 after 140 days of operation.

Two 17.8 cm ID pilot-scale columns designated P1 and P2 were employed during Phase 3 to access the performance of the AnBAC system on a larger scale. The columns, each containing 8.5 kg of virgin 8 x 16 mesh Calgon F-300 activated carbon were placed in operation at the Durez facility in October of 1988. Recycle was provided with a magnetic drive centrifugal pump, while a bellows metering pump was used for feed delivery. Operation of P1 and P2 corresponded to a normal 5 day per week work week. On Saturday and Sunday no influent was delivered to the columns although column recycle and heating were provided continuously. Consequently, the weekly organic loading rate for the pilot scale columns is 5/7 of the daily rate multiplied by seven.

Gas collection in the bench-scale studies was performed with a counter balanced reservoir filled with an acidified salt solution (H₂SO₄/NaCl). Two wet test gas meters were used to measure the gas production from the 17.8 cm pilot-scale columns. Gas production from these columns was adjusted to STP. The correction to STP due to moisture, pressure and temperature differences normally results in a consistent decrease in gas volume of approximately 9 percent. This correction to STP was applied to all the gas production rates. The pertinent features of the three systems are listed in Table 2.

Feed Solutions

The characteristics of the strong liquor wastewater are presented in Table 3. To provide sufficient effluent vol-

ume for sample collection, dilution of the strong liquor with tap water was necessary during the bench-scale studies.

Feed solutions for the Phase 1 and 2 studies varied between 1000 and 6000 mg/L COD and were dependent upon the hydraulic and organic loading rates. The mineral content of the feed was similar to solutions used by Khan, *et al.* [2] and Wang, *et al.* [9]. Feed was prepared by diluting aliquots of strong liquor, salt solution, trace element solution, buffer solution, vitamin solution and L-cysteine solution with tap water in a 20 L glass carboy as delineated in Table 4. The makeup of the various solutions are detailed in Table 5. The feed was degassed with a 30 percent CO₂-70 percent N₂ gas mixture for 20 minutes and then pH adjusted to 7.2 with 50 percent W/W NaOH.

Phase 3 feed was made in a manner similar to the bench-scale feed except that sodium thiosulfate was added to remove residual oxygen rather than the CO₂/N₂ purge. Sodium bicarbonate also was provided to compensate for the carbonate not added by the CO₂/N₂ purging gas mixture.

During Phase 3, the feed solution was modified to reduce precipitation that formed in the feed carboys. Phosphate buffer was reduced so that the effluent pH was close to 7.0 when the influent was maintained at 7.40. The feed pH was adjusted with 50 percent W/W NaOH. The exact composition of the feed depended upon the strength of each particular batch of strong liquor. Shown in Table 6 is the composition of a typical batch of feed. Nutrients were scaled in proportion to the influent COD, with the exception of the sodium thiosulfate and L-cysteine which were provided in proportion to the volume of wastewater.

Methods of Analysis

Analysis for soluble COD was conducted in accordance with *Standard Methods* [1]. The phenol concentration in columns C1-C4 and columns P1 and P2 was measured according to *Standard Methods* S-510C (4-aminoantipyrine method). In columns C1A-C3A, aqueous phenol was measured with a Hewlett Packard 5890 gas chromatograph equipped with an FID detector and a 10 m HP-FFAP column. Chromatogram integration was performed with a HP3396A integrator. Gas quality was measured with a Tracor 560 gas chromatograph equipped with a TCD, a 3.2 mm by 3.3 m SS column with Carbosieve II 100/120 packing and a Perkin Elmer LCI-100 integrator.

TABLE 3. STRONG LIQUOR CHARACTERISTICS

Parameter	Concentration	COD Equivalent
Phenol, mg/L	10,000 to 12,000	23,800 to 28,600
Formaldehyde, mg/L	2,000 to 3,000	2,130 to 3,200
Methanol, mg/L	2,000 to 2,500	3,000 to 3,750
Theoretical COD, mg/L		28,900 to 35,550
COD, mg/L	32,000 to 40,000	
pH, pH units	3.35 to 3.43	

TABLE 4. BENCH-SCALE FEED SOLUTIONS: PHASES 1 AND 2

Feed Solution	Salt Solution mL	Trace Element Solution mL	Phosphate Buffer Solution mL	Vitamin Solution mL	L-Cysteine HCl Solution mL
1000 mg/L COD	150	150	300	6.5	0.93
2000 mg/L COD	150	150	300	6.5	0.93
3000 mg/L COD	250	250	350	10.	1.5
4000 mg/L COD	300	300	350	13.	1.86
6000 mg/L COD	450	450	500	19.5	2.64

Experimental Results

Results obtained from the experimental studies are presented in two sections. Presented first are data representing periods of optimal performance collected during each of the three phases of AnBAC operation. In the second section, data are presented which help illustrate the importance of startup procedures on AnBAC process performance.

Optimal Performance Data

Phase 1: Columns C1-C4: In Phase 1, performance of the AnBAC process when treating the strong liquor was accessed using organic loading rate as the primary operational variable. Organic loading rate was varied by changes in the flowrate and influent COD concentration. During Phase 1, influent COD concentrations of 1,000, 2,000 and 4,000 mg/L and influent flowrates of 0.5, 1.0, and 2.0 mL/min were employed. The above combinations of influent COD and flowrate resulted in organic loading rates ranging from 0.0175 to 0.0618 g COD/g GAC-day. Influent COD concentrations of 1,000, 2,000, and 4,000 mg/L corresponded to influent phenol concentrations of approximately 275, 550, and 1,100 mg/L, respectively.

Data collected during optimal performance periods for each of the studied COD loading rates are presented in Table 7. Optimal performance periods in Table 6 were selected based on consistent performance achieved during the listed time periods. At loadings of approximately 0.03 g COD/g GAC/day, greater than 94 percent COD removal was obtained independent of HRT or influent concentration. At COD loadings of approximately 0.06 g COD/g GAC/day, the highest loading studied, performance levels dropped to 91, 84 and 50 percent. Effluent phenol levels were not measured regularly, but when measured on several occasions gave results less than 0.5 mg/L.

TABLE 5. FEED SOLUTION COMPONENT COMPOSITION

Solution	Component	Mass Added to 2 liters of Solution, g
Salt Solution	(NH ₄) ₂ SO ₄	12.202
	(NH ₄)Cl	113.7
Trace Element Solution	FeCl ₃ · 6H ₂ O	2.493
	MnCl ₂ · 4H ₂ O	0.364
	ZnCl ₂	0.252
	CoCl ₂ · 6H ₂ O	0.2200
	Na ₂ B ₄ O ₇ · 10H ₂ O	0.0880
	Na · Citrate	13.582
	(NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O	0.1600
2 M Phosphate Buffer Solution	K ₂ HPO ₄	464.
	KH ₂ PO ₄	182.
Vitamin Solution	5 grams AH Robins Z-BEC vitamins in 125 mL strong liquor, 125 mL distilled H ₂ O, stir 24 hours at 50°C, centrifuge to eliminate undissolved vitamins.	
L-Cysteine HCl Solution	100 mg/L	

Poor performance of column C1 from day 450 to 513 when loaded at 0.0593 g COD/g GAC/day is thought to be attributable to the past operating history as will be described in a subsequent section. The 84 percent removal achieved by column C3 between day 380 and 427 is a result of the maximum capacity of the column being exceeded at that point in time. Note that during a later time period, the removal capacity of C3 increased to 91 percent. This improved performance is attributed to the increases in C3 biomass concentration which occurred during the intervening time period.

Gas production expressed as the ratio of methane gas produced at STP per gram of COD degraded also is presented in Table 7. The results for the bench-scale studies have been adjusted to STP by applying a nine percent reduction to the measured gas volume as discussed in the Materials and Methods section. The methane content of the offgas throughout the three phases of the study varied between 65 and 85 percent for mature columns at all operating conditions. An offgas methane concentration of 75 percent by volume was used to calculate the methane/COD ratios presented in Table 7. The ratios in Phase 1 ranged from 0.24 to 0.28 L CH₄/g COD degraded. This value is slightly lower than the expected ratio based on conventional stoichiometry. Stoichiometry in the absence of microbial growth predicts 0.35 L CH₄/g COD removed.

Phase 2: Columns C1A-C4A: Process performance of the two inch AnBAC columns in Phase 2 was similar to that achieved in Phase 1. The columns were operated at the same organic loading rates used in Phase 1 but were achieved with higher influent COD concentrations. Higher influent COD concentrations resulted in longer hydraulic residence times for Phase 2 columns. An average influent COD concentration of 6,000 mg/L was used throughout Phase 2 studies. Influent phenol concentrations during Phase 2 averaged 1,650 mg/L.

COD removal efficiencies of 95 percent and greater were achieved during Phase 2 at loading rates ranging

TABLE 6. PILOT-SCALE FEED SOLUTIONS: PHASE 3

Component	Amount
Strong Liquor COD = 39,650 mg/L	100 liters
(NH ₄) ₂ SO ₄	18.6 grams
(NH ₄)Cl	143.9 grams
FeCl ₃ · 6H ₂ O	18,933 grams
MnCl ₂ · 4H ₂ O	2,764 grams
ZnCl ₂	1,915 grams
CoCl ₂ · 6H ₂ O	1,669 grams
Na ₂ B ₄ O ₇ · 10H ₂ O	0.670 grams
(NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O	1.213 grams
Na ₂ S ₂ O ₃ · 5H ₂ O	0.044 grams
K ₂ HPO ₄	410. grams
KH ₂ PO ₄	162. grams
NaHCO ₃	159. grams
AH Robins Z-BEC vitamins	14.5 grams
100 mg/L L-Cysteine HCl Solution	2.5 mL

TABLE 7. PERIODS OF OPTIMAL PERFORMANCE FOR ANBAC PROCESS

Column	Days	Flowrate ml/min	Hydraulic Retention hours	Organic Loading g COD/g GAC/day	Influent COD mg/l	Effluent COD ⁽¹⁾ mg/l	Effluent Phenol mg/l	Percent COD Removal	Gas Produc- tion Rate l/day	Ratio of CH ₄ to COD Removed l @ STP/g COD
Phase 1: C1-C4										
C1	450-513	1.00	15	0.0593	4100	2030 (20)	—	50	1.09	0.24
C2	230-270	1.00	15	0.0322	2244	86 (17)	0.4 (1)	96	1.11	0.23
C3	240-300	1.00	15	0.0175	1214	51 (22)	<0.1 (2)	96	0.58	0.22
C3	380-427	2.00	7.5	0.0588	2042	323 (13)	—	84	1.98	0.25
C3	548-560	2.00	7.5	0.0618	2142	200 (5)	—	91	2.00	0.23
C4	270-300	0.50	30	0.0337	4490	238 (9)	0.3 (1)	95	1.22	0.25
C4	450-498	0.50	30	0.0300	4121	240 (16)	—	94	1.13	0.26
Phase 2: C1A-C4A										
C1A	111-129	0.33	112	0.0099	6264	296 (5)	—	95	1.89	0.42
C1A	129-140	0.66	56	0.0214	6766	246 (4)	2.0 (2)	96	3.30	0.34
C2A	90-140	1.00	37	0.0303	6466	165 (14)	—	97	3.91	0.27
C3A	111-129	0.33	112	0.0097	6264	126 (5)	—	98	2.00	0.44
C3A	129-140	0.66	56	0.0217	6766	212 (4)	<0.1 (2)	97	3.17	0.32
C4A	288-302	4.11	9	0.0590	2992	281 (15)	0.9 (2)	91	6.43	0.27
Phase 3: P1-P2										
P1	206-240	2.27	220	0.015 ⁽²⁾	39000	632 (20)	0.3 (19)	98	33.84	0.38
P2	206-240	3.03	165	0.020 ⁽²⁾	39000	758 (20)	1.0 (19)	98	37.68	0.32

⁽¹⁾ () = number of COD samples.

⁽²⁾ Loading occurs on a 5 day/week basis.

from approximately 0.01 to 0.06 g COD/g GAC/day. Based on these results the maximum removal capacity of the AnBAC process was not exceeded during this phase. Effluent phenol concentrations for column C3A were less than 0.1 mg/L when measured between days 129 and 140. Effluent phenol concentrations from column C1A were higher (2.0 mg/L) during the same period, however column C1A was not at equilibrium but, rather, was undergoing bioregeneration as will be discussed later in this paper.

The methane/COD removed ratio given in Table 7 for column C2A (0.29) is similar to the ratios determined for the Phase 1 columns. Methane/COD removed ratios for columns C1A and C3A, however, are much higher than those found for Phase 1 and are greater than would be predicted by stoichiometry, which suggests conversion of previously adsorbed substrates. The primary difference in operation of column C2A versus columns C1A and C3A was during startup. Both C1A and C3A experienced difficulty during startup which resulted in buildup of phenol and other waste constituents on the GAC particles. It is hypothesized that although the columns approached stable performance in terms of effluent quality during the reporting period of 111 to 129 days, previously adsorbed substrate was continuing to be metabolized and converted to methane. If this hypothesis is accurate, one would expect the gas/COD ratios to decrease as stable column operation continued. This expectation is supported by the reduction of the methane/COD ratios observed for C1A (from 0.45 to 0.36) and C3A (from 0.47 to 0.34) during the next operating period which lasted from 129 to 140 days of operation. If Phase 2 columns had been operated for a longer period, it is hypothesized that further reductions in this ratio would have occurred until they approach the ratios observed in Phase 1.

Phase 3: Columns P1-P2: In Phase 3, undiluted strong liquor was used as the influent source. The undiluted strong liquor has a chemical oxygen demand of approximately 32,000 to 40,000 mg/L and a phenol concentration range of approximately 10,000 to 12,000 mg/L. After an initial period of startup difficulty, the 17.8 cm pilot-scale columns have been operated successfully for approximately 200 days. Detailed performance summaries at these loading rates are presented in Table 7. Currently the columns are operating at higher loadings, but the column operation at these rates has not yet stabilized.

COD removal efficiencies of 98 percent have been achieved at organic loading rates of 0.015 and 0.020 g COD/g GAC/day for the pilot-scale columns. Because of its inhibitory nature and predominance among the three major waste constituents, phenol has been measured daily during the pilot-scale studies. Based on the data presented in Table 7, phenol removals of greater than 99 percent are being achieved at this time. It is expected that as the pilot-scale column operation further stabilizes, the effluent concentration will be reduced below the current values of between 0.3 and 1.0 mg/L.

The methane/COD removed ratio measured to date in the pilot-scale studies are close to or exceed the predicted stoichiometric value of 0.35. Accordingly, using the same reasoning presented during the description of the Phase 2 bench scale results, previously adsorbed substrates are being converted to methane during the performance period reported.

Summary: In Figure 2, COD removal rate is plotted against COD loading rate for data collected during optimum performance periods. As shown, there is consistency between the data collected during the different study phases. Based on the data collected, COD removals

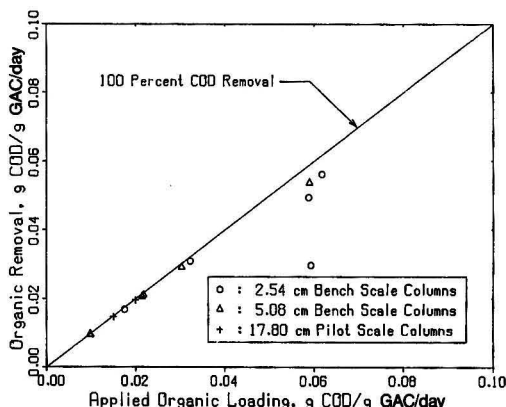


Figure 2. Organic removal rate as a function of applied organic loading expressed as g COD/g GAC/day.

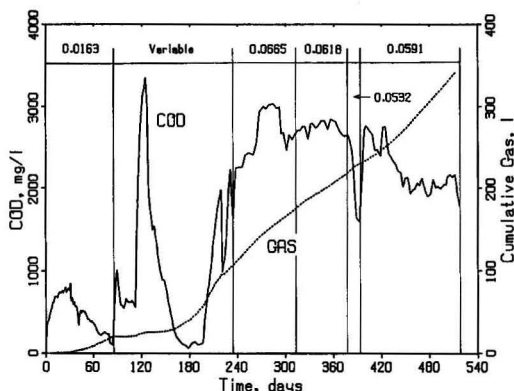


Figure 3. AnBAC column C1 effluent COD and cumulative gas production as a function of time. Organic loading rates as g COD/g GAC/day are indicated on the upper portion of the figure.

of approximately 95 percent and greater can be maintained when the AnBAC process is operated at loading rates of 0.03 g COD/g GAC/day. This loading rate is at least 50 percent greater than previously studied loading conditions listed in Table 1.

Loadings 300 percent greater than reported in Table 1 from previous AnBAC studies of inhibitory wastewaters also have been investigated. At loadings of approximately 0.06 g COD/g GAC, column performance is reduced, which may be indicative that loadings of this magnitude are near the maximum removal capacity of the process. However, under steady conditions, 91 percent soluble COD removal was achieved at 0.06 g COD/g GAC/day.

AnBAC Process Startup

A crucial step in implementing AnBAC processes for inhibitory wastes is process startup. The importance of column startup on the ultimate AnBAC process capacity is highlighted in this section.

Phase 1: Column C1 and C3: The importance of proper startup on eventual AnBAC process performance is most evident when examining performance data from the bench-scale columns C1 and C3. Chronological histories of column C1 and C3 representing effluent COD and cumulative gas production are presented in Figures 3 and 4, respectively. Chemical oxygen demand loading rates expressed as g COD/g GAC/day are indicated in Figures 3

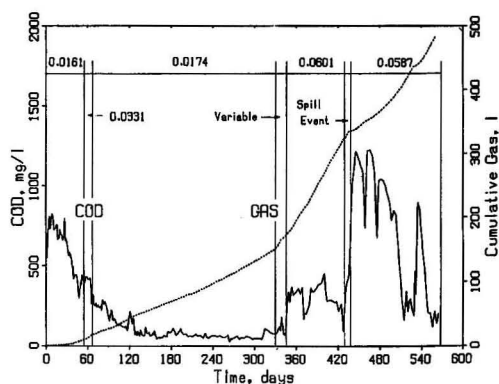


Figure 4. AnBAC column C3 effluent COD and cumulative gas production as a function of time. Organic loading rates as g COD/g GAC/day are indicated on the upper portion of the figure.

and 4 for operational periods. The operating history is explained further in Tables 8 and 9 for columns C1 and C3, respectively.

In reviewing the early operational history of column C1, four attempts were made to increase the loading to 0.058 g COD/g GAC/day as discussed in Table 8. These attempts resulted in poor COD removal and decreases in the gas production rate. Phenol buildup in the column resulted in inhibitory conditions which in turn retarded the biomass growth rate. Consequently bacterial population densities in column C1 remained low.

Column C3 was subjected to an entirely different initial operational protocol. From day 69 to 329, a COD loading rate of 0.0174 g COD/g GAC/day was applied to column C3. During this period of consistent operation no buildup of phenol (measured as COD) occurred and significant biomass growth developed on the carbon as a result of non-inhibitory conditions.

The effect of these differing startup protocols can be seen by inspecting the performance data collected for columns C1 and C3 after day 347 of operation. At this time, both columns were operating at a loading rate of approximately 0.06 g COD/g GAC/day. For column C3, COD removal at this loading rate was excellent (with the exception of the spill event on day 438 of operation) from day 347 to 565. Prior to the spill event (days 380-427) average effluent COD levels of 323 mg/L (84 percent removal) were achieved in column 3. After the column recovered from the spill event, COD removal in C3 averaged 91 per-

TABLE 8. SYNOPSIS OF COLUMN C1 OPERATION

Day of Operation	Average Organic Loading Rate g COD/g GAC/day	Synopsis of Operation
1-84	0.0163	After initial seeding, column operation started at a loading of 0.015. During this period, effluent COD increased and then decreased as column operation became more stable. Noticeable gas production was observed.
85-234	variable	During this time period four attempts were made to increase the organic loading rate to 0.058. Each time this change was initiated (days 85, 112, 197, 224) effluent COD increased dramatically and gas production was inhibited.
235-371	0.0642	Column operation was maintained at 0.06. While performance was relatively steady, percent removal during this period was poor, less than 50 percent.
378-385	0.0532	Organic loading during this period was reduced due to error in feed composition from day 378 to 385. Hydraulic detention was constant, but influent strength dropped from 4000 mg/L COD to 2700 mg/L. An immediate improvement was noticed in performance.
385-513	0.0591	Column loading was resumed at 0.06. A gradual improvement in effluent quality occurred during this time.

TABLE 9. SYNOPSIS OF COLUMN C3 OPERATING HISTORY

Day of Operation	Average Organic Loading Rate g COD/g GAC/day	Synopsis of Operation
1-56	0.0161	After presaturation and startup, loading was 0.014. During this period, effluent quality improved steadily and gas production increased.
56-68	0.0331	Loading to Column C3 increased to 0.03. Good operational stability was observed during this period with effluent COD values remaining steady and variable gas production.
69-329	0.0174	Loading to Column C3 decreased to 0.015 to assess optimal treatment performance.
330-346	variable	Column loading transitioned from 0.015 to 0.06 over a two week period. Column response was excellent.
347-437	0.0601	The best performance at the highest loading was observed during this period.
438-442	N.A.	Major spill event occurred in Column C3, exposing GAC to atmosphere.
443-565	0.0587	Recovery of Column C3 from spill event. Performance gradually improved to that which existed prior to the upset.

cent between days 548 and 560. Conversely, the effluent COD from column C1 was greater than 2000 mg/L (less than 50 percent removal) during this same time period.

The differing startup strategies are hypothesized as the primary reason for the different performance capabilities noted between columns C1 and C3. The increased biomass levels achieved in column C3 during the long period of non-inhibitory operation is thought to be directly responsible for that column's capacity to transition successfully from an organic loading rate of 0.0174 to 0.0601 g COD/g GAC/day. Column C1, which was subjected to inhibitory phenol levels throughout its operation, was never able to achieve performance levels comparable to that of C3, although stable operation was achieved.

Phase 3: Column P1 and P2: Further evidence for the importance of maintaining non-inhibitory substrate levels during startup was obtained during operation of the pilot-scale AnBAC columns. To enhance startup of the pilot-scale system, each column was seeded three times with 2 liters of POTW anaerobic digester mixed liquor and one time with 1 liter settled sludge from the four 2.54 cm bench scale columns (C1-C4) during the first month of operation. After approximately three months of operation it was apparent that—based on the increasing effluent COD concentration and low gas production rate (as shown in Figures 5 and 6 for columns P1 and P2, respectively)—the columns were incapable of successful operation at their initial loading rate of 0.01 g COD/g GAC/day.

During this time, the aqueous phase phenol concentrations increased to 500 mg/L for P1 and 800 mg/L for P2, with corresponding loadings on the activated carbon.

To mitigate the damage caused by the inhibitory phenol concentrations in columns P1 and P2, a buffered nutrient solution containing no strong liquor was fed to the column until the COD of the effluent elutriate was 1000 mg/L. At the end of the elutriation, each column was re-seeded daily for two weeks with 2.5 liters of AnBAC effluent from the 5.08 cm bench scale columns (C1A-C4A). After one month of operation at a loading rate of 0.003 g COD/g GAC/day, gas production rate increased which was taken as an indicator of healthy column operation.

Since then, the organic loading rate applied to columns P1 and P2 has been increased gradually. Increases in the organic loading rate have been consistent with the temporal removal capacity of the process which is dictated by the system biomass development. This approach has resulted in stable column performance and excellent removal efficiency. The current organic loading rate is 0.035 g COD/g GAC/day for columns P1 and P2. This organic loading rate was first applied on day 240 of operation. However, on day 250 the scrubber process that generates the strong liquor was shut down for maintenance which required a loading reduction to the columns. After receipt of new strong liquor on day 289, the columns were placed back in their current loadings.

Summary: As shown in both the bench- and pilot-scale

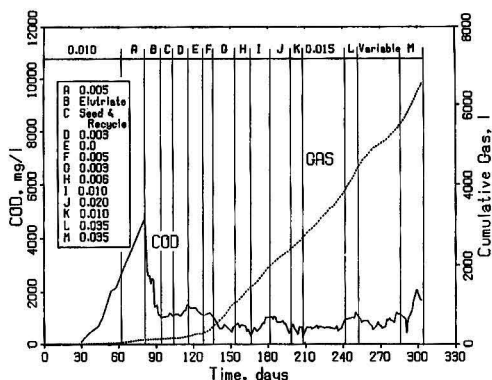


Figure 5. AnBAC column P1 effluent COD and cumulative gas production as a function of time. Organic loading rates as g COD/g GAC/day are indicated on the upper portion of the figure.

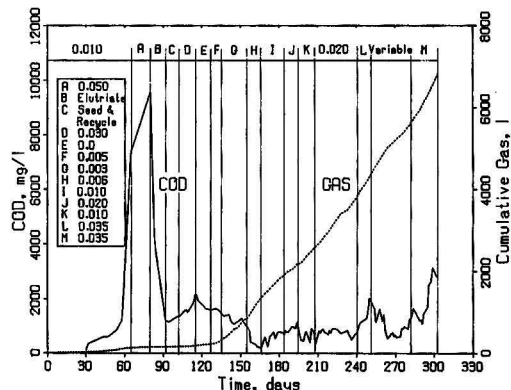


Figure 6. AnBAC column P2 effluent COD and cumulative gas production as a function of time. Organic loading rates as g COD/g GAC/day are indicated on the upper portion of the figure.

studies, care must be taken to ensure stable column operation during startup. Startup is especially critical for inhibitory wastes because improper startup procedures may result in poor initial performance and possible reduction in long term operational capacity as observed in bench-scale column C3. These inhibitory periods, if severe enough, can cause complete process failure. In this study, the optimal AnBAC system performance was obtained from columns not stressed with inhibitory concentrations of phenol. Inhibitory concentrations of phenol were minimized by maintaining organic loading rates consistent with the system's temporal removal capacity.

CONCLUSIONS

Feasibility of the AnBAC process for treatment of a high strength inhibitory wastewater has been successfully demonstrated. Stable operation with excellent organic removal was obtained at organic loading rates higher than reported previously in the literature. At a loading rate of 0.3 g COD/g GAC/day soluble long term COD removal of greater than 94 percent was obtained, with methane production close to the stoichiometric amount. Phenol removal in the pilot facilities exceeded 99 percent.

The organic loading rate limits for anaerobic biological activated carbon (AnBAC) systems also were examined in this study. On a carbon mass basis, organic loadings in excess of 0.06 gram COD/gram GAC/day were studied. In column C3, which was loaded at an organic capacity that never exceeded its assimilation capacity, COD removal efficiency reached 90 percent. To achieve optimal performance at these high loading rates, it was found that the anaerobic bacteria must be allowed to grow under non-inhibitory conditions on the activated carbon for a period of close to one year. Efforts to speed up the growth process by increasing the organic loading rate resulted in inhibitory phenol concentrations, long term reduction in process efficiency, and possible process failure.

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Separation of Hazardous Organics by Reverse Osmosis Membranes

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Extensive experimental studies showed that thin-film, composite membranes can be used effectively for the separation of selected hazardous organic compounds. This waste treatment technique offers definite advantages in terms of high solute separations at low pressures (<2 MPa) and broad pH operating range, and the use of charged membrane would allow the selective separation of some organics from feeds containing high salt concentrations. In addition, feed pre-ozonation of selected organics has been shown to provide significant improvement in flux and rejection characteristics for both charged and uncharged membranes due to the formation of ionizable organic acid intermediates during the ozonation that do not interact as strongly with the membrane. It has been shown that the overall ozonation-membrane process could be greatly effective in producing permeate water of high quality while minimizing the volume of waste that must be further treated. Batch adsorption studies were also utilized to understand the membrane flux drop phenomena in non-ozonated solutions.

INTRODUCTION

Chemical manufacturers generate millions of tons of wastes containing various hazardous priority pollutants each year. The development of alternative technologies for the treatment of various hazardous wastes is becoming increasingly important as concerns grow over its disposal. These and other wastes, such as leachate from unsecured disposal sites, contain a wide variety of priority pollutants

such as pesticides, herbicides, PCBs, chlorinated hydrocarbons, and heavy metals. Much of this waste is relatively dilute and so must be concentrated before further treatment [1, 2].

Several methods have been used for the treatment of dilute wastewater. These include biological treatment, stripping, and carbon adsorption [3, 4]. Ozonation has also been found to be effective in oxidizing some hazardous organics [5, 6] to less toxic compounds. Membrane processes can be used to purify wastewater and produce a 20 to 50 fold decrease in waste volumes that must be treated with other processes such as incineration or wet air oxidation, greatly reducing energy cost.

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Membrane processes are gaining considerable attention for the purification and volume reduction of dilute hazardous wastes. The development of low pressure reverse osmosis (RO) membranes such as aromatic polyamide and sulfonated polysulfone has resulted in membrane processes which give high water flux at low pressures (<2MPa). These thin-film, composite membranes can provide high solute separations and have definite advantages in terms of energy savings, capital cost, and broad pH (2 to 12) operating range. The low pressure membranes can provide simultaneous separation of hazardous organics and inorganics. Selective separations of ionizable compounds are also possible with membranes containing charged groups [7, 8].

Membrane performance is measured in terms of membrane rejection (R), permeate water flux (J_w), and extent of water recovery (r). The rejection is a measure of solute separation by the membrane and is defined as

$$R = 1 - \frac{C_p}{C_i}$$

where C_p and C_i are the solute concentrations in the permeate and feed streams, respectively.

Reviews of the development of membrane technology can be found in Sirkar and Lloyd [9], Sourirajan and Matsuura [10], Lee [11], and Belfort [12]. Although many of the applications referred to in these involve the use of cellulose acetate membranes, works with thin-film, composite membranes were more favorable for the separation of hazardous wastes. Chian, *et al.* [13] used reverse osmosis systems to remove more than 99% of fifteen major pesticides. Carcinogenic substances were removed 92.5% with both spiral wound and hollow fiber polyamide membranes in studies by Light [14]. Shrem and Lawson [15] used reverse osmosis units to treat wastewater from an organic chemical manufacturing plant and found organic matter rejection over 90%. Bhattacharyya, *et al.* [16, 17] have done extensive work with various priority organic pollutants using thin-film aromatic polyamide (FT30) spiral wound modules. Experiments with priority pollutants showed that rejections of >98% for PAH compounds (naphthalene, anthracene, phenanthrene) were possible with little drop in permeate water flux. For ionizable organics such as phenol, chlorophenols, and nitrophenols, they found that rejections and flux drops were highly dependent on operating pH values. Membrane rejections (at pH 11) were 99.5% to 99.8% for phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, etc.

Studies have shown that high separations of hazardous organics such as chlorinated phenolics can be achieved by low pressure polyamide membranes. However, these studies have indicated substantial water flux drop for non-ionized chloro and nitrophenols due to membrane-solute interactions [17]. It is known that partial ozonation will convert many chlorinated organics to intermediate organic acids (oxalic, formic, etc.) [5, 6, 18]. These organic acids do not interact as strongly with the membrane and so cause less flux drop. Also, since these intermediates are ionizable, charged membranes can be utilized to achieve high water flux and separation of partially ozonated hazardous organics at low pressures.

OBJECTIVES

This work deals with the use of low pressure thin-film, composite membranes for the concentration and separation of selected chlorophenols and chloroethanes with and without feed pre-ozonation. The two types of membranes utilized in this study were aromatic polyamide (FT30) and carboxylated (negatively-charged) polyamide (NF40) membranes. Membrane feed pre-ozonation will

result in the formation of organic acid intermediates which should result in less flux drop and, since these compounds are ionizable, high separations by charged as well as uncharged membranes. Separation and flux characteristics of both charged and uncharged membranes were studied with both non-ozonated and ozonated (selected chlorophenols and chloroethanes) solutions to evaluate the effectiveness of the ozonation-membrane process for the enhanced removal of priority organic pollutants. Adsorption of non-ionized chlorophenols on two types of membranes were also established by batch experiments.

EXPERIMENTAL

Membrane experiments were conducted with a system (Figure 1) containing both a batch and a continuous flow cell so that the performance of two different membranes could be studied at the same time. The thin-film, composite membranes used in the experiments were the Film Tec NF40 and the FT30-BW; the NF40 was placed in the batch cell and the FT30 in the flow cell. The pump shown in the system served to provide flow of solution through the continuous cell and mixing in the batch cell; compressed nitrogen was used to supply the pressure driving force for the system. The operating conditions were: system pressure (P_{avg}) of 0.3-1.4 MPa, feed pHs of 3.0-9.4, and system temperature of 24°C.

The procedure used for experiments involving ozonation-membrane process is outlined in Figure 2. Membrane feed solutions were ozonated in a 1.8 liter stirred reactor with a flow of 0.20 standard liters per minute (SLPM) O_2 containing 2% ozone. Pre-ozonation times ranged from 0 to 60 minutes. After ozonation, solutions were mixed for several hours to allow decomposition of residual ozone. Membrane experiments were then carried out with the ozonated solutions.

Membrane performance was measured in terms of flux drop from that of distilled water flux (DWF) and solute rejection. Membrane feed, concentrate, and permeate samples were analyzed by Total Organic Carbon (TOC) and HPLC direct injection. TOC was measured using a Beckman Model 915-B Carbon Analyzer. HPLC analysis (phenolics) was performed with a Varian 5000 liquid chromatograph using a MCH-5 column (reverse phase octyldecylsilane on silica) and a UV-50 variable detector at 220 and 280 nm.

RESULTS AND DISCUSSION

Membrane separation of selected hazardous organics with and without feed pre-ozonation were investigated with the NF40 and FT30-BW membranes. Single component studies were conducted with trichlorophenol while multicomponent systems examined consisted of trichlorophenol/humic acid mixtures and mixtures of chlorophenol, dichlorophenol, trichlorophenol, trichloroethane, and tetrachloroethane. A wide range of ozonation times and pressures were studied, and, since many of the compounds studied were ionizable, several membrane feed pH values were investigated. Membrane performance results are presented in terms of solute rejection and flux drop. The % flux drop (at a particular pressure) is defined as:

% Flux drop =

$$\frac{\text{Distilled Water Flux} - \text{Flux with Wastewater}}{\text{Distilled Water Flux}} \times 100$$

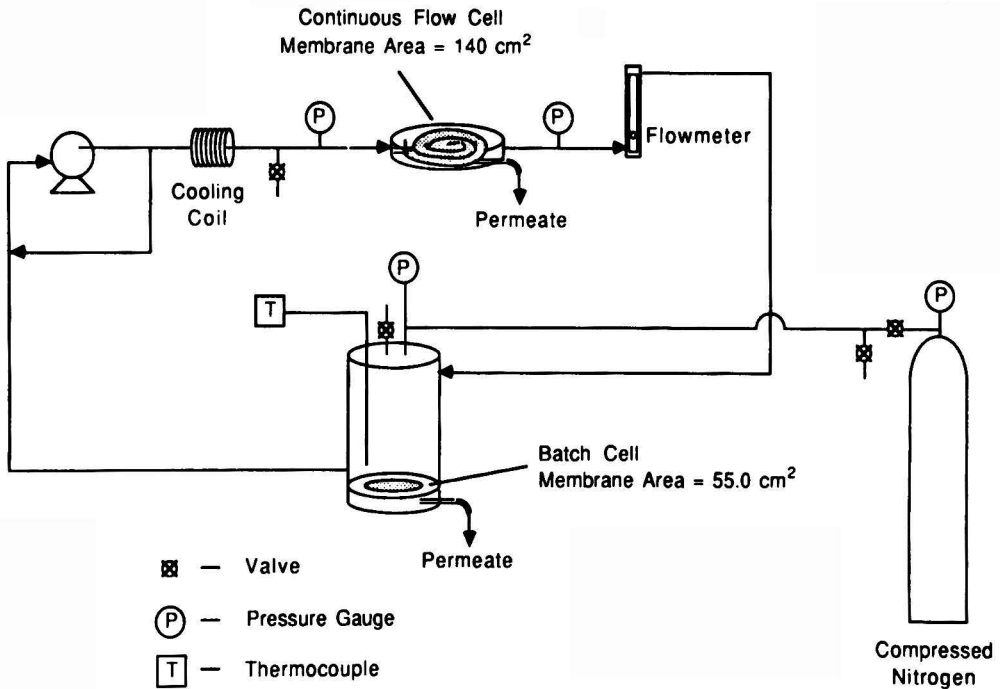


Figure 1. Schematic of system for membrane experiments.

Membrane stability was checked by standard sodium chloride and sodium sulfate rejections and distilled water fluxes. For the NF40, a negatively charged nanofiltration membrane made of carboxylated polyamide, the DWF at 1.38 MPa was found to be $11 \times 10^{-4} \text{ cm}^3/\text{cm}^2\text{s}$ (23.3 gal/ft² day). Sodium chloride and sodium sulfate rejections were 30% and 97%, respectively. The DWF of the FT30, an aromatic polyamide membrane, was also $11 \times 10^{-4} \text{ cm}^3/\text{cm}^2\text{s}$ at 1.38 MPa; sodium chloride and sodium sulfate rejections for this membrane were 96% and 97%. The low sodium chloride rejection of the NF40 illustrates the principal advantage of the charged membrane over reverse osmosis membranes such as the FT30. The FT30 membrane gives high rejections of most solutes, whereas the NF40 mem-

brane can be used to selectively separate compounds with different charges.

Studies with Trichlorophenol

Membrane feed solutions of 50 mg/L trichlorophenol (TCP) were ozonated from 0 to 60 minutes. The pH of the solutions decreased after ozonation; this drop in pH indicated the degradation of the TCP to intermediate organic acid compounds. HPLC analysis indicated that after 5 minutes of ozonation the TCP concentration was reduced to 24.7 mg/L, and after 15 minutes, was <0.5 mg/L. Formation of carbon dioxide during the ozonation was indicated by reduction in TOC and the presence of carbon

OZONATION OF SOLUTION

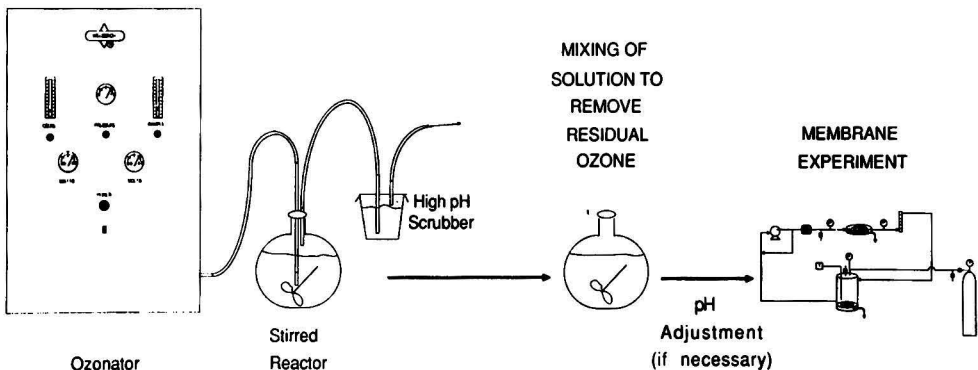


Figure 2. Schematic of ozonation process for ozonation-membrane experiments.

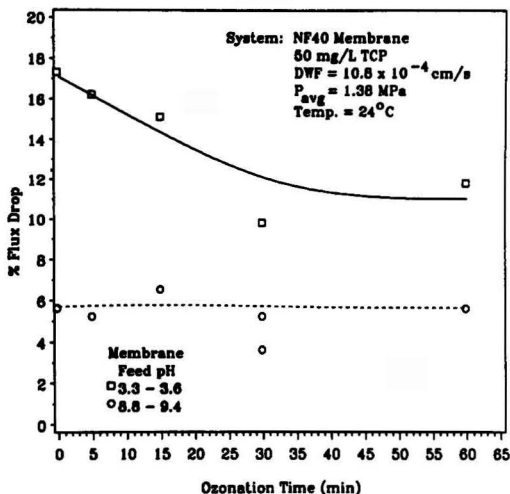


Figure 3. Effect of ozonation on flux drop for the NF40 membrane with trichlorophenol.

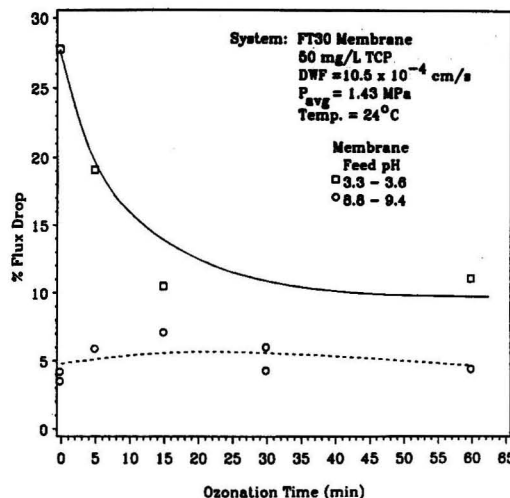


Figure 5. Effect of ozonation on flux drop for the FT30 membrane with trichlorophenol.

dioxide in the high pH trap placed after the ozonation reactor.

Figure 3 shows flux drop as a function of ozonation time for the NF40 membrane for low (3.3-3.6) and high (8.8-9.4) pH membrane feeds. At low feed pH, TCP is not ionized and so interacts strongly with the membrane; the adsorbed TCP displaces water in the membrane pores, causing significant water flux drop. Ozonation of TCP results in the formation of organic acids which do not interact as strongly with the membrane, and so cause less flux drop. At the high feed pH the TCP is ionized; the negatively charged solute does not interact as strongly with the charged membrane and the flux drop is less than that at the lower feed pH. Since the ozonation products are also ionizable, the flux drop for ozonated solutions are also smaller under the high pH conditions.

TOC rejections for the NF40 membrane are shown in Figure 4. It can be seen that both an increase in feed pH and ozonation time increased rejections. An increase in feed pH results in the ionization of the TCP or the organic acid intermediates formed during ozonation. These nega-

tively charged species are more highly rejected by the negatively charged NF40 membrane. Ozonation improves rejection since the organic acids that are formed ionize at lower pHs than does TCP and so these are rejected better than TCP at lower feed pHs.

Figures 5 and 6 show the flux drop and TOC rejection for the FT30 membrane. Under non-ionized conditions (feed pH 3.3-3.6), the TCP interacts strongly with the membrane, causing a large flux drop. The drop in water flux is greater than that for the NF40; the charge on the NF40 weakens the interactions between the TCP and the membrane. As with the NF40, ozonation reduces flux drop for the FT30 membrane by reducing solute interactions with the membrane. Under ionized conditions (feed pH 8.8-9.4), the TCP and organic acids formed during ozonation do not interact with the FT30 membrane as strongly as under non-ionized conditions and so the flux drop is smaller. Figure 6 shows that feed pH and ozonation did not greatly affect TOC rejection for the FT30 membrane; this membrane does not depend on charge for separation as does the NF40 membrane.

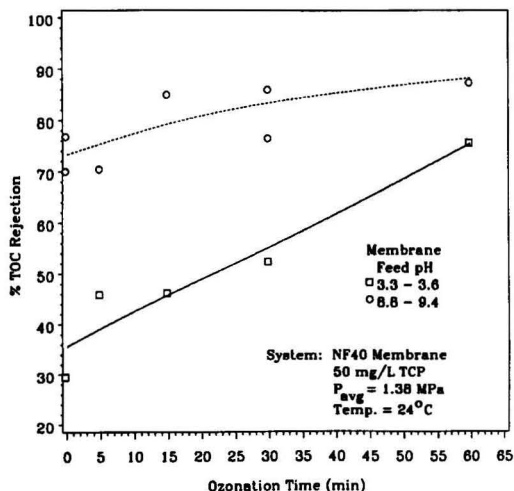


Figure 4. Effect of ozonation on TOC rejection for the NF40 membrane with trichlorophenol.

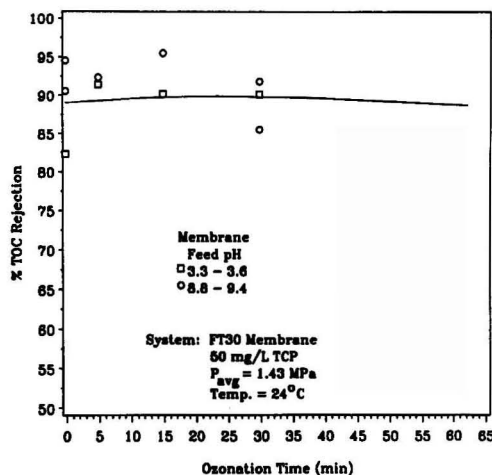


Figure 6. Effect of ozonation on TOC rejection for the FT30 membrane with trichlorophenol.

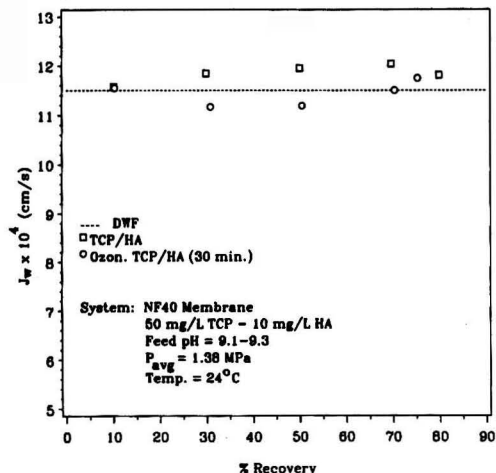


Figure 7. Flux as function of water recovery for the NF40 membrane with trichlorophenol/humic acid mixtures.

Studies with Trichlorophenol/Humic Acids

Experiments to determine the effect of water recovery on water flux and solute rejection were conducted with mixtures of 50 mg/L trichlorophenol and 10 mg/L humic acids (TCP/HA). Humic acids are high molecular weight compounds that are present in soils and so can be found in ground water containing hazardous organic leachates. These compounds are highly rejected by the membrane but can cause large water flux drops due to adsorption.

The fluxes for distilled water, TCP/HA, and TCP/HA ozonated for 30 minutes are given in Figure 7 as a function of water recovery for the NF40 membrane. For both non-ozonated and ozonated TCP/HA, no drop in flux was observed even at high recoveries; the TCP/HA and the organic acids formed during ozonation were ionized at the high feed pH (9.1-9.3) and so little change in water flux occurred. The TOC rejections are shown in Figure 8. Rejection of the non-ozonated TCP/HA decreased from 80% at 10% recovery, to 64% at a recovery of 80%; however, for the ozonated solution, 84% TOC rejection was

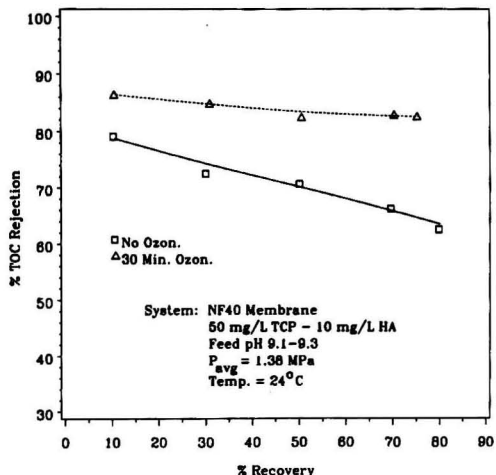


Figure 8. TOC rejection as function of water recovery for the NF40 membrane with trichlorophenol/humic acid mixtures.

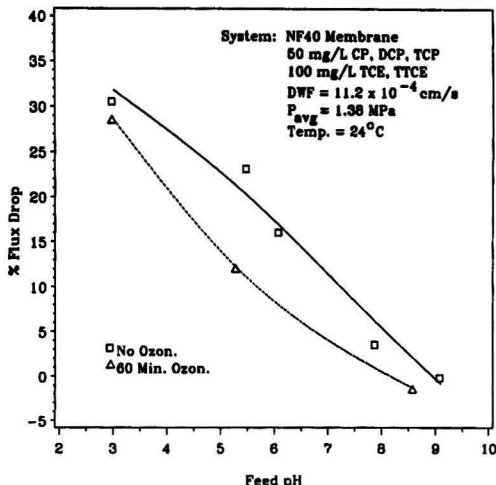


Figure 9. Effect of feed pH and ozonation on flux drop for the NF40 membrane with hazardous organic mixtures.

maintained even at 75% water recovery. The decrease in TOC rejection for the non-ozonated TCP/HA could have been the result of enhanced concentration of the HA at the membrane surface. Since degradation of the HA is expected during ozonation, HA concentration on the membrane surface did not increase for the ozonated solution, and TOC rejection remained high.

Studies with Mixtures

Studies were performed with mixtures of 50 mg/L chlorophenol (CP), dichlorophenol (DCP), and trichlorophenol (TCP) with 100 mg/L trichloroethane (TCE) and tetrachloroethane (TTCE) to determine the effect of multicomponent systems on flux and TOC rejections for ozonated and non-ozonated solutions. The flux behavior of the mixture with the NF40 was found to be linear over the pressure range 0.34-1.38 MPa (50-200 psi), indicating the absence of surface polarization phenomena. Flux drops as a function of pH for the NF40 membrane at 1.38 MPa are shown in Figure 9. Flux improves substantially with an increase in feed pH for both the ozonated and non-ozonated mixtures; ozonation did not greatly improve flux drops found for the mixture at a fixed feed pH. However, Figure 10 shows that TOC rejection is enhanced significantly for the mixture after ozonation for 60 minutes. While the non-ozonated mixture rejection is almost constant for the different feed pHs, it is increased to as high as 80% for the ozonated mixture. The increase is due to the formation of organic acids which ionize and are rejected by the membrane. Although the phenolics in the mixture are ionizable, the pKa of these compounds are much higher than those of the intermediates, and also, the chloroethanes present are not ionizable. As a result, the rejection of the non-ozonated mixture did not increase over the pH range studied. However, the organic acids, formed after ozonation, have much lower pKa's and so are rejected by the charged membrane.

The flux behavior of the mixture with the FT30 membrane was also found to be linear over the pressure range studied. FT30 membrane flux drops and rejections are shown in Figures 11 and 12 for an operating pressure of 1.43 MPa. Flux drop is also a strong function of feed pH for this membrane, and feed pre-ozonation does improve flux drop over the range of feed pHs studied. As with the

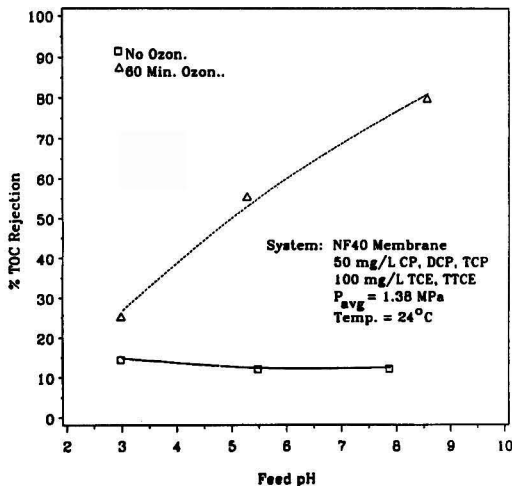


Figure 10. Effect of feed pH and ozonation on TOC rejection for the NF40 membrane with hazardous organic mixtures.

single component TCP system, ozonation produces intermediates that do not interact with the membrane to the same extent as the mixture and so flux is enhanced. TOC rejection slightly increases with ozonation and feed pH.

Overall Removal of Trichlorophenol

Figure 13 illustrates an example calculation of an ozonation-membrane process for the separation of hazardous organics; trichlorophenol is used as the model compound. After ozonation for 30 minutes the TCP concentration would be reduced to <0.2 mg/L; the TOC of the feed solution would be 66 mg/L due to the formation of carbon dioxide during the ozonation. For a membrane that rejects 90% (either the NF40 or FT30), the permeate contains only 6.6 mg/L TOC which would be due primarily to organic acids; the TCP concentration in the permeate would be less than 0.2 mg/L. For 90% water recovery, the concentrate TOC, also mostly due to organic acids formed during ozonation, would be 1194 mg/L. This

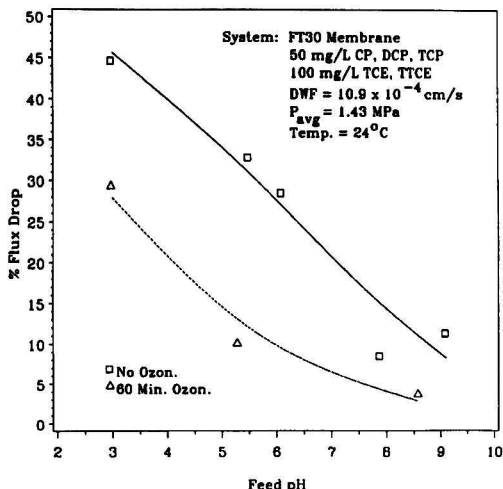


Figure 11. Effect of feed pH and ozonation on flux drop for the FT30 membrane with hazardous organic mixtures.

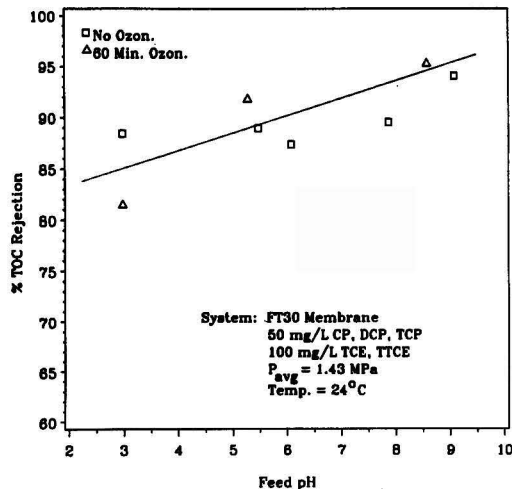


Figure 12. Effect of feed pH and ozonation on TOC rejection for the FT30 membrane with hazardous organic mixtures.

greatly reduced volume could be disposed of by incineration. The overall ozonation-membrane process would produce permeate water of high quality (overall TCP removal of $>99.8\%$) and greatly reduce the volume and risk of waste that must be further treated. Also, since the process has been shown to be effective when utilizing charged membranes, selective separation of hazardous organics from feeds containing high salt concentrations would be possible, allowing high fluxes at low operating pressures even for feeds with high osmotic pressures.

ADSORPTION OF CHLOROPHENOLS ON MEMBRANES

Several authors have reported a certain amount of unaccounted (membrane adsorption) feed organics in the material balance of all streams of reverse osmosis [13, 16, 17]. Chian *et al.* [13] have studied the reverse osmosis of several pesticides and reported adsorption of solutes on membranes as calculated from the material balance. These adsorbed solutes cause a reduction in the permeate flux and hence it is important to understand the nature of the adsorption to be able to solve the problem of flux drop in the membranes. Bhattacharyya and Madadi [16] have modeled the fouling due to organics adsorption of chlorophenols using a numerical solution.

There has been no attempt, however, by these researchers to perform experiments directly to obtain the amount of solutes adsorbed on the membrane. In the present work batch adsorption studies of some priority hazardous organics has been studied. The solutes studied included 2-chlorophenol (CP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). The membranes used were the aromatic polyamide FT30 membrane and the carboxylated polyamide NF40 membrane. The experiments were carried out by selecting a membrane area, weighing it, and contacting it with a mixture of chlorophenols for 24 hours. The concentration of the adsorbate was 0.25 mM of each species.

Results of adsorption experiments show some interesting trends. The adsorption isotherms of chlorophenols mixture adsorption of FT30 and NF40 membranes are shown in Figures 14 and 15. The adsorption data fit the Langmuir isotherm equations with a high degree of correlation. The trend of curves is the same for adsorption of chlorophenols on the FT30 and NF40 membranes. The

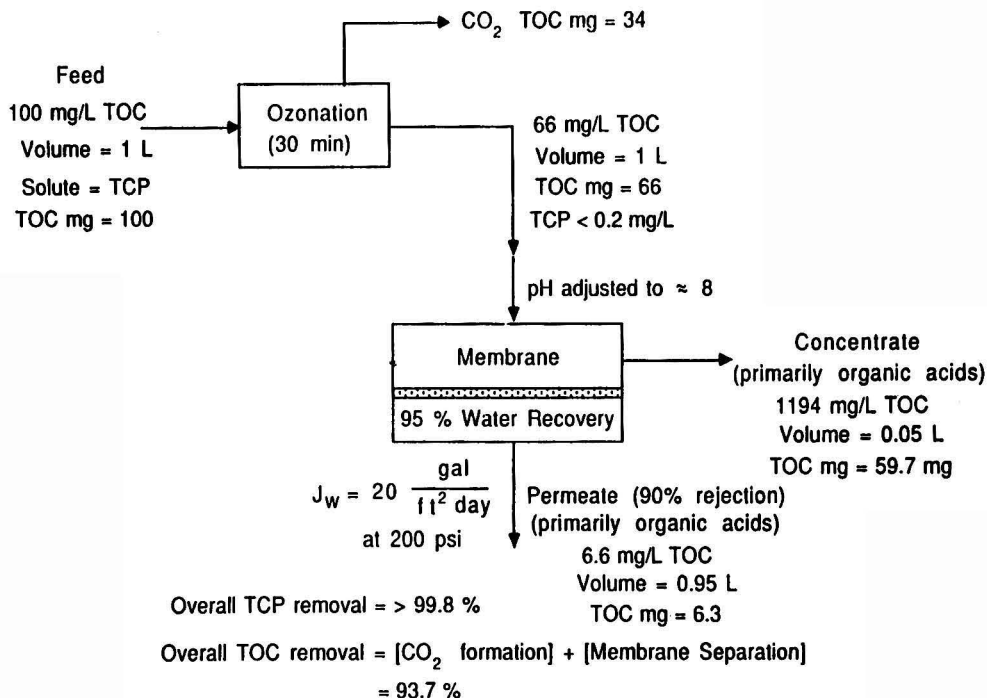


Figure 13. Example calculation of ozonation-membrane process.

amount of TCP adsorbed per unit weight of the membrane is the highest followed by the amount of DCP adsorbed per unit weight. The amount of CP adsorbed per unit weight is the least in the three solutes. The same sequence is followed for the NF40, *i.e.*, TCP > DCP > CP. The relative amounts of each solute adsorbed on the membrane is the same for adsorption on different membranes.

The adsorbate solution pH plays an important role in the adsorption process. The adsorption was higher at non-ionized conditions, *i.e.*, pH < pKa for the solutes, and the amount of solute adsorbed decreased with increase in pH with respect to the dissociation constants of the solutes.

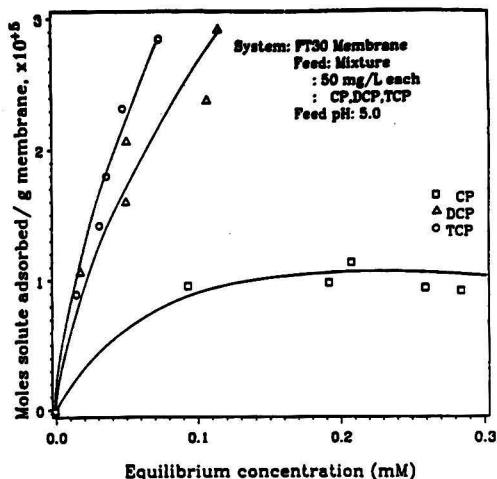


Figure 14. Adsorption isotherms of chlorophenols on FT30 membrane with mixtures at pH 5.0.

The pH effect on adsorption can be modeled by considering that only the non-ionized molecules take part in the adsorption process. This effect of pH on adsorption trend was similar for single solute solution adsorption as well as for multicomponent mixtures.

The amount adsorbed from a solution of the single solute was significantly higher than the amount adsorbed from a mixture of solutes. Thus the other solutes hinder the adsorption process. Changing the solvent from aqueous to 30% methanol-70% water (vol/vol) solution decreased the amount of solutes adsorbed. The methanol-water solution has more affinity for solutes than the affinity of distilled water for these solutes.

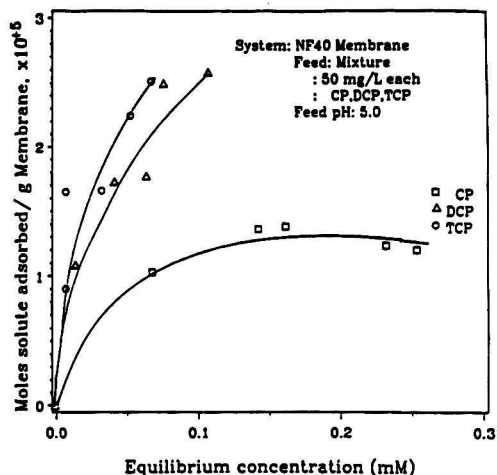


Figure 15. Adsorption isotherms of chlorophenols on NF40 membrane with mixtures at pH 5.0.

The amount of solute adsorbed in actual reverse osmosis experiments showed similar trends. The amount of TCP adsorbed was the highest, followed by DCP; the amount of CP adsorbed was the least on a unit membrane area basis. The results of the batch type adsorption studies correlated well with the hydrogen bonding parameter and other physicochemical parameters such as net adsorption energy and connectivity index [19]. Hence, it can be shown that the amount of solutes adsorbed in actual membrane runs is proportional to the amount of solutes adsorbed in batch adsorption experiments. The flux drop in reverse osmosis treatment of dilute hazardous organics has been related to the amount of solutes adsorbed in the reverse osmosis runs [16, 17, 20]. Hence, if batch adsorption data are available, membrane flux drop can be predicted.

CONCLUSIONS

The separation of dilute hazardous organics by two types of thin-film, composite polyamide membranes has been shown to be an effective technique. Also, the separation characteristics of the organics by the membranes were shown to be improved by feed pre-ozonation. The two membranes studied, a charged nanofiltration membrane (NF40) and a low pressure reverse osmosis membrane (FT30), had water fluxes of $10\text{--}13 \times 10^{-4}$ cm/s at 1.4 MPa; NaCl and Na₂SO₄ rejections were 30% and 97%, respectively, for the NF40 membrane and 96% and 97%, respectively, for the FT30 membrane. For the ionizable compounds (chlorophenols) studied, flux drops were highly dependent upon feed pH. The NF40 membrane flux drop was 17.4% at feed pH 3, but <6% at pH 9 for trichlorophenol, and over 30% at pH 3—while only 3.7% at pH 7.9 for a chlorophenol-chloroethane mixture. The FT30 membrane flux drop with trichlorophenol decreased from 27.9% at pH 3 to 4.3% at pH 9.4, and from 44.8% at pH 3.0 to <12% at pH >7.9 for the chlorophenol-chloroethane mixture. Feed pre-ozonation reduced flux drop of both membranes for trichlorophenol and the chlorophenol-chloroethane mixture below feed pH 6. Rejections of the NF40 membrane increased from 29.8% to over 70% for trichlorophenol as feed pH was increased from 3.4 to >9; TOC rejections of the chlorophenol-chloroethane mixture by the NF40 membrane were <15%. For the same mixture, the FT30 membrane TOC rejections were in the range of 80% to 96%. Ozonation improved the NF40 membrane rejection to as high as 87.6% for trichlorophenol and to over 80% TOC rejection for the chlorophenol-chloroethane mixture. Humic acids present in trichlorophenol solutions did not affect separation characteristics of the two membranes. It was shown that the ozonation-membrane process could remove > 99.8% of the hazardous organic trichlorophenol and 93.7% of the TOC. Batch adsorption experiments were also conducted to understand membrane flux drop behavior. The adsorption trend was found to be in the order: TCP > DCP > CP.

ACKNOWLEDGMENT

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Overview of Industrial Source Control for Nitrogen Oxides

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Contemporary debate over major clean air issues has kept the control of nitrogen oxides (NO_x) in the forefront of public interest. While amendments to the Clean Air Act, new rules, programs, and policies emerge in response to concern for acid deposition, ozone non-attainment, global warming, and public health and welfare, it is anticipated that NO_x control technology will be applied to a greater degree. However, existing regulations, policy and market forces are already forcing technological advances. This article presents a summary of the current regulatory situation and looks ahead at the Clean Air act reauthorization. The article also presents an overview of stationary source control for NO_x emissions.

CURRENT REGULATORY FORCES

Federal Statutes

New Source Performance Standards (NSPS) and Prevention of Significant Deterioration (PSD) regulations may dictate the type and level of NO_x abatement to be achieved on facilities with the potential for NO_x emissions. NSPS set emission limits for NO_x (and other criteria pollutants) for specifically defined new, modified, or reconstructed affected facilities. Table 1 lists the NSPS that pertain to NO_x emission sources. NSPS establish minimum requirements for applicable facilities, regardless of source location or air quality impact. Recently, the U.S. EPA has broadened the applicability of NSPS, as in the decision to consider "nonroutine" repairs proposed by Wisconsin Power Company (WEPCO) to restore deteriorated steam equipment to past operating capacity as an "increase in emissions." This determination set a precedent since WEPCO's proposal did not involve an expenditure of 50% of the replacement value, modification of pollution controls, an increase in permitted emission rates, or an increase in the plant's historical operations. [1].

PSD review is required for modified or new "major sources" of NO_x emissions that are located in areas designated as attainment or unclassifiable for National Am-

bient Air Quality Standards (NAAQS). A major source is defined as that with the potential to emit 100 tons or more per year of any pollutant regulated under the Clean Air Act (CAA)—see Table 2—or any source with the potential to emit 250 tons or more per year of any CAA pollutant. A major modification is defined as causing the facility to become a major emission source or causing a net significant emission increase at a major source. Under PSD regulations, each pollutant emitted in significant quantities (e.g., 40 tons per year for NO_x) must undergo analyses including:

- Best Available Control Technology (BACT) determination.
- Ambient Air Monitoring (or use of existing monitoring data).
- PSD increment consumption analysis.
- NAAQS analysis.
- Class I and non-attainment area impact analysis.
- Analysis of the impact on soil, vegetation, and visibility.

The BACT determination involves the selection of a control technology that will result in the maximum reduction in pollutant emissions considered achievable using current technology. Energy requirements, environmental impacts, and economic impacts should be considered in the BACT determination.

TABLE 1. NEW SOURCE PERFORMANCE STANDARDS FOR STATIONARY SOURCES OF NITROGEN OXIDES

Subpart D	- Fossil Fuel-Fired Steam Generators for which construction commenced after August 17, 1971.
Subpart Da	- Electric Utility Steam Generating Units for which construction commenced after September 18, 1978.
Subpart Db	- Industrial-Commercial-Institutional Steam Generating Units.
Subpart Dc	- (Proposed) Small Industrial-Commercial-Institutional Steam Generating Units.
Subpart Ea	- (Proposed) Municipal Waste Combustors.
Subpart G	- Nitric Acid Plants.
Subpart GG	- Stationary Gas Turbines.

BACT review is a technology-forcing process, *i.e.*, each new or modified emission source should apply or improve upon the technology used by preceding applicants. The EPA maintains a clearinghouse of previous BACT determinations for this purpose. To ensure that progress is made in improving technologies, the EPA has further adopted an aggressive "top-down" approach for conducting a BACT determination, which presumes the most stringent available control technology to be BACT unless an applicant satisfactorily demonstrates otherwise. This approach requires applicants to identify the most effective control technology (regardless of cost, applicability to the source, or commercial availability), and assess the feasibility of using the technology for the applicant's emission source. If the most efficient technology is not justified (on the basis of a substantial or unique technical, environmental, or economic basis), the applicant then evaluates the second most effective technology. The review process continues until the appropriate control technology and level of abatement is selected. However, it is possible that PSD sources may require a level of control better than that of BACT, to meet air quality impact criteria (*e.g.*, Class I impacts, PSD increment, or NAAQS analysis). Again, the level of control implemented by such new or modified facilities establishes a new precedent and a baseline for expectations for future similar industrial sources.

State Implementation Plans

As defined in State Implementation Plans, new major emission sources or source modifications located in designated non-attainment areas have to employ Lowest Achievable Emission Rate (LAER) technology and obtain emission offsets for the non-attainment pollutant. LAER is defined as the most stringent emission limitation which is contained in the federal implementation plan of any state for such class or category or source, unless the owner or operator of the proposed source demonstrates that such limitations are not achievable. In the absence of source specific rules, LAER is the most stringent emission limitation which is achieved in practice by such class or category of source. Emission offsets refer to the reduction of emissions of the same pollutant either within the same facility or at a nearby facility. The offset requirements vary from one air quality control region to another. Generally, emissions must be reduced by a greater extent than the potential emissions from the proposed source (*e.g.*, a 2 to 1 ratio). Also, the distance from the offset source to the proposed source may be limited by regulation and/or affect the offset ratio. If off-site emission reductions are needed, the cost of obtaining the offsets, if offsets are available, could be high.

The potentially high cost of offsets, or even the unavailability of offsets, may force prospective new facility owners or owners of planned source modifications to employ

TABLE 2. 100 TON PER YEAR PSD SOURCE CATEGORIES [2]

1. Fossil fuel-fired steam electric plants of more than 250 million Btu/hr heat input.
2. Coal cleaning plants (with thermal dryers).
3. Kraft pulp mills.
4. Portland cement plants.
5. Primary zinc smelters.
6. Iron and steel mill plants.
7. Primary aluminum ore reduction plants.
8. Primary copper smelters.
9. Municipal incinerators capable of charging more than 250 tons of refuse per day.
10. Hydrofluoric acid plants.
11. Sulfuric acid plants.
12. Nitric acid plants.
13. Petroleum refineries.
14. Lime plants.
15. Phosphate rock processing plants.
16. Coke oven batteries.
17. Sulfur recovery plants.
18. Carbon black plants (furnace process).
19. Primary lead smelters.
20. Fuel conversion plants.
21. Sintering plants.
22. Secondary metal production plants.
23. Chemical process plants.
24. Fossil fuel boilers (or combinations thereof) totalling more than 250 million Btu/hr heat input.
25. Petroleum storage and transfer units with a total storage capacity exceeding 300,000 barrels.
26. Taconite ore processing plants.
27. Glass fiber processing plants.
28. Charcoal production plants.

extraordinary emission control strategies to reduce facility emissions to below levels that would trigger the need for offsets. Non-attainment areas for NO_x are limited to certain regions of California. However, the role of NO_x emissions as a precursor to ozone formation has raised some question among air pollution control agencies as to the possible need for applying LAER for NO_x sources in ozone non-attainment areas. This position has been embraced by several air pollution control districts in California that have pronounced ozone non-attainment problems.

Finally, general provisions within State Implementation Plans have been used by some regulatory agencies as a very effective mechanism for advancing the practice of industrial NO_x emission control when Federal regulations do not apply or are not considered sufficiently stringent. States have varying acronyms for requiring the use of recent improvements in technology, such as those below:

- Pennsylvania—Best Available Technology (BAT).
- Tennessee—Best Available Control Technology (BACT).
- New Jersey—Advances in the Art of Control Technology.

The exact application of these requirements varies. For example, source-specific policies may or may not have been published. Also, energy, economic, or other environmental impacts may or may not be considered (and if so, it is not always clear how much weight will be given to these concerns). Hence, the general provisions of State Implementation Plans may be the overriding factor in defining a required level of control.

Some states have embraced interstate planning in recognition of the regional nature of air shed problems. For example, the Northeast States Coordinated Air Use Management (NESCAUM) has issued policy to its member states establishing BACT limits. NESCAUM's BACT guidance for gas turbines (9 ppmv NO_x firing gas, 25

ppmv NO_x firing oil) goes well beyond NSPS limits (75 ppmv NO_x firing gas), and practically dictates the use of selective catalytic reduction technology to achieve the prescribed level of control.

CLEAN AIR ACT REAUTHORIZATION

In June 1989, President Bush presented his Clean Air Plan designed to curb acid rain, urban air pollution, and toxic air emissions. Among other primary provisions, the plan called for:

- A 2 million ton reduction in NO_x by the year 2000.
- NO_x reductions to be achieved may be less than 2 million tons, provided that 12 million tons in acid rain causing pollutants (I.E., NO_x or SO₂) are reduced by 2000. Utilities may trade reductions of NO_x for reductions of SO₂ or vice versa.
- Emissions trading among electric plants within a state or within a utility system would be allowed in order to meet a 5 million ton reduction by the end of 1995, and full interstate trading would be allowed in order to meet the 12 million ton acid gas emission reduction by the year 2000.

The House of Representatives and the U.S. Senate are now considering vastly different mark-ups of the Administration's plan. Since the introduction of H.R. 3030 and S. 1630, much debate, closed door negotiations, and bipartisan compromise has occurred. Key congressmen and senators are shifting their negotiating position routinely. As of this writing, it is not possible to project the final format of provisions pertaining to NO_x reduction, as several compromise bills and hundreds of amendments are being discussed and proposed in both houses. Voting is expected to begin soon, however the amendments will not likely be passed into law until the fall of 1990 or later. It should be anticipated that the final amendment will call for NO_x reduction at least as significant as the Bush proposal and possibly greater. The net impact to industry may be additional and more stringent NSPS, applicability of PSD and State regulations for smaller sources, and greater enforcement action.

NO_x CONTROL TECHNOLOGY

This section briefly outlines the potentially available NO_x control technologies in a typical "top-down" format, i.e., most stringent first. The alternative systems for control of NO_x are: wet flue gas denitrification (FGDN), selective catalytic reduction (SCR), reburning, selective noncatalytic reduction (SNCR), combustion technology, electron beam, and fuel switching or source separation. The applicability and cost of these techniques varies for different combustion units. Some of the variations are highlighted.

Flue Gas Denitrification (FGDN)

FGDN systems use common wet scrubbing techniques to react absorbed SO₂ with NO to form molecular nitrogen. However, because NO is basically insoluble in water, additional chemicals are added first to bring the NO into solution, followed by the NO/SO₂ scrubbing process. Chemicals used for this purpose are water-soluble ferrous-chelating agents, ozone, sodium chlorite, and chlorine dioxide. Handling of the latter two chemicals can pose significant safety risks.

The major drawbacks to the use of an FGDN process include expensive chemical additives, high water usage,

and variable SO₂ levels with some fuels such as municipal solid waste (MSW). Some recent pilot studies with metal chelates (particularly iron EDTA) have indicated NO_x removals of 70% to 90%, utilizing techniques such as an electrolytic cell to maintain reactivity or high temperature regeneration [3]. Comparable simultaneous SO₂ removal can be achieved. The targeted application of this developing technology is coal-fired utilities.

Selective Catalytic Reduction

SCR processes use a catalyst bed and anhydrous ammonia (NH₃) for removal of NO_x emissions. NH₃ is injected into the flue gas upstream of the catalyst. Intimate mixing occurs between the injected ammonia and flue gas NO_x (predominantly in the form of NO). This mixture then passes over the catalyst bed and reacts to form diatomic nitrogen and water (provided the reaction temperature is approximately 600°F–700°F).

Most SCR experience is in Japan and Western Europe where NO_x removal has ranged from 85% to 90%. SCR has been used with success on gas turbines and is planned for fluidized bed cogeneration facilities in the United States; however, in the U.S., SCR has not yet been used for coal-firing or MSW. Experience with European coal-fired installations suggests that transfer of the Japanese technology to United States design and operating practices may not be straightforward [4]. Domestic coal and MSW present other problems to available catalysts. For example, catalyst attack by acid gases requires the use of innovative special acid-resistant catalysts. The catalysts presently available on a commercial basis are sensitive to particulate and sulfur products. Thus, usually the catalysts would have to be installed downstream of acid gas and particulate controls. As a result, the flue gas stream would no longer be at the optimal reaction temperature. Either catalysts must be used that would be effective at low temperatures or else substantial energy costs will be incurred for flue gas reheat prior to NO_x removal. Low temperature acid-resistant catalysts can only be termed to be in advanced development stages, rather than commercially available.

Catalyst development continues toward increasing applicability. The Englehard and Norton companies have each developed a zeolite SCR catalyst for NO_x control at temperatures up to 950°F. The W. R. Grace Company is developing dual function SCR catalysts for both CO and NO_x control and also SO₂ and NO_x control [5].

Reburning

Reburning could achieve 50% to 60% NO_x reductions as well as some control of organic emissions. Reburning diverts 10% to 20% of the heat input to create a second combustion zone that is oxygen-deficient and encourages reduction to N₂. Reburning can be accomplished with any fossil fuel fired source, but NO_x emissions are lowest with natural gas. A demonstration is underway for coal-fired boilers with sorbent injection. MSW incinerators may be less suited for reburning—as an energy penalty could be incurred and modification of air flows may be required. The most likely application will be for retrofitting coal-firing or cyclone boilers.

Selective Non-catalytic Reduction

SNCR involves ammonia or urea injection, but not in the presence of a catalyst. Two major SNCR systems are commercially available: the Exxon Thermal DeNO_x am-

monia injection system and the Fuel Tech NO_xOUT urea injection system. A third system, the Emcotek Two-Stage DeNO_x urea/methanol injection system, has undergone extensive pilot testing and a full scale demonstration on one MSW incinerator line in Switzerland. These systems are discussed in the following subsections.

Ammonia Injection

Exxon Thermal DeNO_x ammonia injection, like SCR, uses the NO_x/ammonia reaction to convert NO to molecular nitrogen. However, without catalyst use or supplemental hydrogen injection, NO_x reduction reaction temperatures must be tightly controlled between 1600°F and 2200°F (between 1600°F and 1800°F, for higher efficiency). Below 1600°F and without hydrogen also being injected, ammonia will not fully react, resulting in what is called ammonia breakthrough. If the temperature rises above 1800°F, a competing reaction begins to predominate, resulting in increased NO_x emissions. Therefore, the flue gas region where ammonia is injected must be selected to ensure that the optimum reduction reaction temperature will be maintained.

Thermal DeNO_x is an available technology that has been used primarily on gas-fired boilers and gas turbines and may achieve NO_x removals as high as 70% to 80% within the narrow temperature range noted previously. Thermal DeNO_x has also attained 40% to 60% removals on commercial installations of oil and coal-fired utility boilers, glass furnaces, and MSW incinerators.

However, there is generally some "slip" of ammonia which does not react completely and which can cause odors, fouling, and a visible plume. Thermal DeNO_x has an additional disadvantage in that the storage and handling of anhydrous ammonia may cause safety problems.

Urea Injection

The Electric Power Research Institute (EPRI) discovered and patented the chemical process of using urea (CO(NH₂)₂) to convert nitrogen oxides to nitrogen and water. This process of urea injection has been further developed and is being marketed by Fuel Tech, Inc. as the NO_xOUT process.

Urea injected alone has a high NO_x reduction activity between 1700°F and 1900°F. With process enhancers and adjusted concentrations, the NO_xOUT process is effective from 1500°F–2100°F. Enhancers alone are used between 1000°F and 1500°F. The NO_xOUT system can be utilized at temperatures above 2100°F by introducing dilution water to cool the gas stream to within desired temperature ranges. A 50% urea solution is typical but solutions as low as 10% may be used. To optimize NO_x reduction, different urea and chemical enhancer solutions may be injected at different temperature levels.

Ammonia may form in this process and react with sulfur compounds to form ammonia salts. The ammonia salts can potentially foul heat recovery equipment. In the NO_xOUT process, free ammonia is controllable by specific chemical enhancers which act as ammonia scrubbers.

The NO_xOUT process is generally deemed impractical for application to NO_x sources with large load variations and also to gas turbines. The applicability to turbines and other sources may be feasible in the future, pending development of new chemical enhancers and commercial demonstration experience.

Commercial applications employing the NO_xOUT process for post-combustion NO_x control have been made at a pulverized brown coal-fired boiler, a refinery gas-fired CO boiler, and a pulverized coal utility boiler. These applications have demonstrated NO_x reductions of 35% to

70%. Both coal-fired commercial applications were in Europe. A number of applications have also been tested on pilot units.

Urea/Methanol Injection

Emcotek has developed and patented the Two-Stage DeNO_x process, which utilizes both urea and methanol injection. Emcotek's initial pilot studies on a 1 MW crude oil boiler used methanol alone to remove NO_x. The final patent involves separate injection of both urea and methanol through proprietary nozzle designs. In this process, the primary function of the methanol is to reduce ammonia slip and air preheater deposits.

The Two-Stage DeNO_x system has been installed, operated, and tested at one 330-TPD, 24-year-old line of the KVA Basel MSW incineration facility, which has heat recovery [6]. The system reportedly achieved NO_x reduction between 65% and 80% of the uncontrolled level of 160 ppm (dry) at flue gas temperatures between 1500°F and 1900°F. Ammonia slip was below 5 ppm for flue gas temperatures greater than 1600°F and reportedly can be maintained below 1 ppm. NO_x reductions of 78%, 65%, and 48% were achieved at urea to NO_x molar ratios of 0.80, 0.60, and 0.40, respectively. The KVA Basel installation was the first full-scale demonstration of the Two-Stage DeNO_x system. The first commercial applications are currently being installed or proposed.

Combustion Technology

Because of the abundance of nitrogen in coal and MSW, NO_x formation is primarily a function of excess air (provided oxygen is available) and combustion temperature. For natural gas and low-nitrogen oil, NO_x is also formed at high temperature from the nitrogen in the fuel and the oxygen in combustion air. Combustion modifications that reduce NO_x emissions include reducing the available oxygen at critical stages in the combustion, lowering the peak flame temperature, and reducing the residence time during which nitrogen is oxidized. These combustion parameters can be controlled by automatic systems to maintain combustion within the operating range that will minimize NO_x production. Combustion design features, such as low NO_x burners, low excess air, water/steam injection, staged combustion, combustion air introduction, flue gas recirculation and waterwall combustor designs, as well as operating practices (*i.e.*, control of temperature and oxygen availability in various combustor regions), can be used to reduce NO_x by 20% to 60%.

Various combustion modification techniques have been found to be cost effective for different combustion technologies. Utilities have achieved 20% to 30% NO_x reduction with low excess air, biased firing, burners-out-of-service (*i.e.*, alternate burner firing), and 40% to 60% reduction with low-NO_x burners and overfire air. Gas turbines have achieved 40% to 80% reduction with water/steam injection. Industrial boilers utilize low-NO_x burners and other techniques used by utilities. MSW incinerators use waterwall combustors or internal flue gas recirculation designs, as well as automated combustion controls, to reduce NO_x emissions.

Electron Beam

The Electron Beam (E-Beam) process is an innovative technique that has been tested on a pilot-scale at utilities. Ammonia or lime is reacted with NO_x and SO₂ in the presence of an electron beam that provides the activation

energy for the NO_x to react. Therefore, higher temperatures, such as those required for SCR and SNCR are not needed. A fabric filter downstream removes reactants. At present, the capital and energy costs of this technology are prohibitive.

Fuel Switching/Source Separation

Switching from high-nitrogen (*e.g.*, coal and some oils) to low-nitrogen (*e.g.*, natural gas) fuels can reduce NO_x emissions, particularly from utility and industrial boilers.

Source separation is possible for waste fuels like municipal solid waste, and involves the removal from the waste stream of materials such as food wastes and yard wastes with a high nitrogen content. For example, yard wastes can be collected separately and composted. Fuel switching and source separation are not always practical or economically feasible.

SUMMARY

Concern for public health and welfare have brought about rules and policies that provide for the increased application of air pollution controls. Continuing concerns

over air quality and acid deposition have lead to new proposed legislation that would require substantial reduction in future levels of nitrogen oxides released from industrial sources to the atmosphere. Enactment of these bills will accelerate the commercial application of available technology.

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PCB Detoxification Technologies: A Critical Assessment

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Management of PCBs under the Toxic Substances Control Act (TSCA) since promulgation of the first regulations in 1978 has cost industry and government over \$1 billion. A significant portion of that expense has been associated with disposal of PCB liquids and PCB articles, ranging from routine PCB removal and replacement to disposal of debris from PCB spills and fires.

Since the first PCB incineration permit was granted by the U.S. EPA in 1979, PCBs have also been one of the most expensive chemicals to dispose of commercially. High prices combined with the limited permitted disposal capacity has prompted scientists and engineers to continue the search for less expensive ways to detoxify PCB-contaminated material. Ironically, these factors have also driven the development of innovative technology for other less expensive waste streams that would otherwise have been passed over.

The search for improved PCB detoxification technology continues as disposal capacity continues to shrink and PCB-related cleanups approach the remediation stage. This paper looks at the state of PCB detoxification technology, reviewing past and present technology development efforts and relating these technologies to the industry's remedial needs in the coming years.

DRIVING FORCES FOR PCB DETOXIFICATION ADVANCES

TSCA regulations stipulate landfill and incineration as the acceptable options for PCB disposal, and include design criteria and destruction targets that are in some ways more stringent than their counterparts for other hazardous wastes under the Resource Conservation Recovery Act (RCRA). Commercial incineration and landfill capacity has been installed and operated for many years, and studies have shown the routine capacity needs of industry are being met by these companies [1].

The uncertainty in PCB disposal capacity and gate price is more of a problem for unusual disposal situations and one time cleanups, such as those required under Superfund or property transfer practice. These unique individual situations have also created needs for special

on-site technology, either in an attempt to minimize remedial costs or because of the impracticality of off-site disposal.

To illustrate this point, compare the list and chronology of approved PCB (stationary) incineration capacity against the amount of alternative disposal developmental work, listed in Tables 1 and 2 respectively [2]. Note that only one stationary incinerator has been permitted for PCB destruction since 1985 (except for capacity expansions), but that more than half of the alternative disposal permit applications have been submitted since then. It is also noteworthy that the majority of recent incineration permit activity has been associated with mobile units, again underlining the trend toward on-site disposal as a solution to unique site-specific problems. However, most of the mobile incineration designs parallel the technology used for stationary combustion [3].

TABLE 1. U.S. EPA APPROVED PCB INCINERATORS

Company	System Type	Location	Regions Approved
Aloca Corp.	Liquid Injection	Davenport, LA	7
APTUS	Rotary Kiln/Liquid Injection	Coffeyville, KS	7
Dow Chemical	Liquid Injection	Freeport, TX	6
	Liquid Injection	Oyster Creek, TX	6
	Liquid Injection	Plauemine, LA	6
Enscoc	Rotary Kiln/Liquid Injection	El Dorado, AR	6
EPA Office of Research and Development	Rotary Kiln/Liquid Injection	Mobile process	2
General Electric	Liquid Injection	Pittsfield, MA	1
	Rotary Kiln	Waterford, NY	2
LaPorte Chemical	Liquid Injection	Pasadena, TX	6
Pyro-Magnetics	Liquid Injection	Mobile process	1, 4, 5, 7, 8, 9
Rollins Environmental Services	Rotary Kiln/Liquid Injection	Deer Park, TX	6
Chemical Waste Management	Rotary Kiln/Liquid Injection	Chicago, IL	5
Tennessee Eastman Company	Liquid Injection	Kingsport, TN	4
Vulcan Materials	Liquid Injection	Geismar, LA	6

One of the major driving forces for new technology development is associated with the relatively stringent standards associated with PCBs in soils and on surfaces. While EPA published its PCB spill cleanup policy in 1987 establishing PCB cleanup standards (10 ppm/25 ppm in soil, 0.1/1.0 $\mu\text{g}/\text{cm}^2$ on surfaces), regional EPA and state policies have in some cases been even more stringent. New Jersey's ECRA precedents for PCB cleanup are in some situations as low as 1 ppm in soil and concrete, resulting in a significant increase in cleanup scope over the EPA spill policy. Soil treatment technologies have encountered greater difficulty in meeting these regional standards on routine cleanups.

On-site treatment and destruction technology is still subjected to significant research for those situations where off-site disposal presents an unacceptable liability

for the generator, and where the scope of cleanup is considered too small to justify large-scale thermal treatment (less than 1000 tons).

In reviewing the driving forces for PCB detoxification development, it is interesting to note the trends in funding associated with these technologies. While much of the original technology investment was generated by the utilities through the Electric Power Research Institute, and by the EPA Office of Research and Development once the TSCA regulations were in place, most of the investment today comes from either private service companies attempting to improve on available systems or through the Superfund Innovative Technology Evaluation (SITE) program in an attempt to address unique Superfund-scale problems. EPRI's research program has involved more than 30 projects and over \$10 million, but their investment today is much less.

TABLE 2. RESEARCH AND DEVELOPMENT (R&D) PCB DISPOSAL APPROVALS

Company	Process	Date Issued
Chemdecon	Chemical	6-29-84
MRI	Dielectric Fluid Combustion Study	9-4-84
Acurex	Physical Separation (Soil)	2-12-85 11-15-85 4-7-86
Rollins	Physical Separation (Capacitors)	5-23-85
OHM	Chemical	7-3-85
AMOP	Physical Separation (Soil)	8-30-85
U.S. Army	Incineration Amended	1-14-85 6-6-86 2-5-86
ERT	Electrochemical	3-20-86
Transformer Consultants	Physical Separation (Transformers)	3-20-86
Shirco	Alternate Thermal	5-13-86
Sunohio	Chemical	6-26-86 10-15-87
PTI	Physical Separation (Solvent flush recovery)	8-1-86 9-17-86
General Electric	Physical Separation (Transformers)	9-25-86
Georgia Power	Solvent Extraction	11-12-86
General Electric	Chemical	5-12-87
IT Corporation	Chemical (<i>In-situ</i>)	5-29-87
	Thermal Separation	2-10-88
U.S. DOE	<i>In-Situ</i> Vitrification	9-11-87
ENSCO	Transformer Disassembly	1-15-88
U.S. EPA/ORD	Chemical	1-21-88

SOIL REMEDIATION TECHNOLOGY

PCB detoxification technology for soil can be described by the following four major categories:

- Thermal treatment.
- Chemical treatment.
- Physical separation.
- Biological treatment.

Thermal Treatment

The most significant investment in PCB detoxification technology by service companies has been in the thermal detoxification/separation technology. Most of this effort has focused on large-scale transportable incineration intended for a wide variety of organic contaminants in soil. Table 3 lists most of the available transportable incineration systems and the scale of projects in which they are involved. Most of the systems involve integrated rotary kiln/afterburner technology, and some have applied for and/or received permission to burn PCB under TSCA [4].

The integrated rotary kiln technology has proved to be the most versatile for multi-waste sites. However, most of these systems suffer from a significant economy of scale, and are generally thought to be cost-effective only for sites containing a minimum of 5000 tons of contaminated soil.

The demand for smaller capacity units has been filled in part by thermal separation systems, which remove the PCB from soil for destruction in an afterburner. Technol-

TABLE 3. AVAILABILITY AND SCALE OF TRANSPORTABLE THERMAL TREATMENT TECHNOLOGY

Incineration Company	Incinerator ¹ Design	Site Type/Name	Approximate Site Size (Tons)
Vesta	Small rotary kiln (RK)	Pesticides, NC	50
		Nyanza, MA	1,500
Incinerex ENSCO	Small RK Medium RK	Delray Beach, FL	2,000
		American Crossarm, WA	1,000
		Delray Beach, FL	2,000
		Sydney Mines, FL	10,000
		Lenz Oil, IL	7,000
Roy F. Weston OH Materials	Medium RK Medium infrared conveyor furnace (IRCF)	NCBS, MS	19,000
		Lauder Salvage, IL	7,500
Haz-Tech/ Westinghouse Ogden	Medium IRCF	Florida Steel, FL	19,000
		Peak Oil, FL	10,000
Bell Pole & Lumber IT Corp.	Medium circulation fluidized bed Medium RK Large RK	Kenai, AK	70,000 ²
		Stockton, CA	10,000 ²
		Bell Pole, MN	20,000 ²
Envirite ENSCO	Large RK Large RK	CAAP, ME	40,000
		LAAP, LA	120,000 ²
		MOTCO, TX	75,000 ³
		Prentis, MS	10,000
		Bros, NJ	100,000 ³

¹ Small rotary kiln - <20 MMBtu/hr; medium rotary kiln = 20-40 MMBtu/hr; large rotary kiln = >40 MMBtu/hr.

² Remediation in progress.

³ Remediation awarded, but not yet started.

ogy options include direct and indirect heating, and in most cases have the potential economic advantage of producing thermally treated soil rather than ash. These systems also suffer from a lesser economy of scale, however, and are typically considered only for projects in excess of 500 tons. They also have been limited in their application to PCBs thus far, and in some cases require some form of vaporization enhancement (*i.e.*, the presence or addition of lighter hydrocarbons). Most thermal separation technologies have therefore seen PCB-related activity only at Superfund sites (where permits may not be required) or as part of alternative technology demonstrations for EPA.

Chemical Treatment

Chemical treatment to remove or detoxify PCB in soil has been the subject of research and demonstration in recent years, primarily due to the desirability of *in situ* remedial options. Demonstration-scale systems have included solvent or detergent washing and detoxification with more conventional PCB dechlorination chemistry (NaPEG, KPEG) [5]. One of the few systems to survive the technology review process to date is the KPEG technology for soil [6]. This system has been the subject of several field demonstrations, and is the technology of choice for several upcoming Superfund remedial projects.

Apart from the physical problems of removing PCB from soil, most soil treatment systems have suffered more from the problem mechanics of soil/liquid separation and hazard classification of the final residue. Only further demonstration on a field production scale will determine whether the soil residue is suitable for replacement at the site, and whether waste water and other waste treatment problems relating to these systems can be remedied in a cost-effective manner [7].

Physical Separation

Physical separation techniques for *in situ* treatment have received significant attention in recent years, due in

part to the growing number of sites where PCB-contaminated soil removal is infeasible due to buildings and other obstructions. *In situ* volatilization (ISV) and *in situ* vitrification techniques have both been considered for PCB removal from unsaturated soil. ISV systems in particular have become common for VOC removal from soil, and in some cases have collected PCB as a byproduct. Because of the low ambient vapor pressure of PCB, however, use of ISV systems for PCB removal will require enhancement in order to achieve the current soil cleanup standards for most sites. Enhancements might include localized vitrification itself, steam injection, or radio frequency heating. Steam injection technology has been increased activity for removal of semi-volatile organic compounds from soil, and at least one patent for steam injection to remove PCBs from soil is pending [8].

Biological Treatment

Biological treatment of PCB continues to be reviewed as a possible complement to other technologies, and is being considered as a long term "polishing" step for several major cleanups where contamination levels are relatively low. While scientists seem to agree that bacterial and fungal dechlorination can occur and could be considered a remedial option, few scientists consider it a large-scale alternative for sites containing more than 25 ppm PCB [9].

PCB CONTAMINATED HYDROCARBON TREATMENT

Incineration has long been considered the most feasible option for most PCB-contaminated hydrocarbons, and in some cases can be the only feasible option for disposal of contaminated water. Stationary and mobile PCB treatment technologies still exist commercially, and prosper in locations where (1) incineration capacity is distant and costly, and (2) the hydrocarbon in question is more expensive to incinerate or has some potential reuse value. Most of the hydrocarbon treatment work to date has fo-

TABLE 4. U.S. EPA APPROVED ALTERNATE METHODS FOR PCB DISPOSAL

Company	Location	Regions Approved
Acurex	Mobile process	Nationwide
Environmental, Int., Inc.	Mobile process	7, 8
Franklin Inst./Philadelphia	Mobile process	3, 6, 8
General Electric	Mobile process	3, 6, 7, 8
PCB Destruction Co.	Mobile process	7
PCB Treatment, Inc.		7
PPM, Inc.	Mobile process	Nationwide
Sunohio	Mobile process	Nationwide
T&R Electric		8
Transformer Consultants	Mobile process	Nationwide
Chemdecon	Mobile process	Nationwide
Environmental Inter., Inc. (Mechanical shredding with extraction)		7
Quadrex (Extraction followed by distillation)		Nationwide

cused on PCB-contaminated mineral oil from transformers, where the treated oil (to 2 ppm) can be used as a fuel or (in some cases) reused as dielectric fluid [10].

Both sodium- and potassium-based systems are available, with sodium systems predominating for transformer oil treatment. Table 4 lists the current permitted alternate disposal systems, most of which are for PCB treatment in mineral oil. The KPEG technology has been developed by several companies in recent years in an effort to improve upon the safety of NaPEG oil treatment and minimize the sensitivity of the treatment process to true waste materials and their contaminants (water in particular). KPEG technology has been proposed for a variety of innovative uses, including special hydraulic oils and PCB-contaminated gas pipeline condensate.

Distillation of PCB-contaminated solvents, while not a detoxification process in itself, requires a permit under TSCA because it "avoids disposal." Most of the solvent distillation technology for PCB has focused on Freon, where the solvent is used as a flushing medium for electrical equipment internals and other mechanical devices such as pipelines and compressors. Conventional distillation technology is employed for this purpose.

PCB CONTAMINATED SOLID SURFACES

Building and equipment decontamination technology for PCBs continues to receive increased focus due to the problems associated with conventional cleaning techniques for concrete and metal. Traditional decontamination methods include solvent or detergent washing, but under certain circumstances these techniques will not achieve the prevailing cleanup standards under the EPA policy or ECRA-type guidelines [11].

Destructive techniques such as shotblasting and scabbling have seen increased application for shallow surface decontamination, as PCBs will generally not migrate far below the surface without the presence of other hydrocarbons. The adaptation of these techniques for traditional floor and wall preparation has also required that special vapor and particulate control equipment be designed to fit these units to both contain PCB-contaminated exhaust and minimize re-entrainment of PCBs in a work space [12].

High-pressure water washing has also been applied to concrete and painted surface treatment as a fast and relatively clean method of removing the outer surface containing PCB. Waste generation is reduced over that of

other washing techniques, and water treatment is straightforward—provided detergents are not used.

Several companies have attempted to develop and commercialize detoxification technology for PCB in concrete, using variations on the same KPEG technology used for contaminated oil and soil. These techniques have seen only limited success on concrete, but continue to be developed as a potentially nondestructive technique for buildings and equipment.

In a similar vein, the endorsement of encapsulation procedures under the EPA spill cleanup policy has spawned increased attention on sealant and resurfacing technology, particularly for concrete surfaces where continued use is desirable. These encapsulants, typically epoxy compounds or polymer concrete, are similar to traditional concrete resurfacing technology, but increased effort is being focused on their ability to resist abrasion, disintegration from other solvents, and diffusion of PCB into and through the sealant. Proper selection and satisfactory application of these sealants may provide an acceptable solution to many concrete contamination scenarios, particularly if recontamination of the surface can be prevented through proper blending and application. The ideal surface treatment for concrete would include both a dechlorination compound and a perpetual sealant blended into one mixture, but little if any activity is currently proceeding along these lines.

GENERAL COMMENTS ON AVAILABLE TECHNOLOGY

The clear focus of PCB detoxification technology development today seems to be on mobile or *in situ* specialty applications where conventional stationary incineration and landfill are impractical or undesirable. As noted earlier, these technologies include:

- Vapor extraction from soil.
- Soil washing or dechlorination.
- Thermal separation from soil.
- Sealing of concrete or *in situ* dechlorination.
- Small-scale on-site treatment in general.

A majority of PCB-related soil projects involve less than 500 tons of soil, a problem for which there is no inexpensive solution. Enhanced vapor extraction or *in situ* dechlorination appear to hold the most promise for this application [13].

The lack of full-scale demonstration experience with many of the technologies also puts a heavy burden on consultants and engineers when attempting to select the appropriate technology for many sites. The most common recommendation in remedial feasibility studies is for off-site PCB disposal, particularly incineration, as landfill liability becomes more of a concern. Few engineers and their clients are willing to invest the time and risk capital for technology demonstration, being particularly reluctant to apply a system that has not advanced beyond the pilot-scale.

Many of the technologies also have associated uncertainties regarding waste treatment and byproducts disposal requirements themselves. Both soil treatment and incineration generate large quantities of byproducts ranging from ash to waste water, some of which has not been fully characterized and will be site-specific in its determination as a hazardous waste. Better definition of waste generation issues is necessary before technology can be applied, particularly for small sites where demonstration is infeasible.

Permit issues are often a concern as well. While application of PCB technology to Superfund sites does not always require a formal TSCA permit, TSCA requirements must still be met and the process of proving the concept

can be costly and time consuming. Classifying a technology as "available" is inappropriate unless all necessary permits have been received and the process is ready for field operation.

The net effect of these drawbacks is that firm pricing (lump sum unit price) is difficult to obtain from most vendors applying on-site technology. While EPA and other government agencies can often afford to apply innovative technology on a demonstration scale, the increase in implementation activity by industry and other responsible parties requires decision making on the basis of firmer unit pricing for technology application based on the prevailing cleanup criteria. Consulting engineers and clients are both reluctant to implement many promising technologies because of the lack of cost information, so PCB technology innovation will be stalled until the implementation knowledge and cost database is expanded.

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