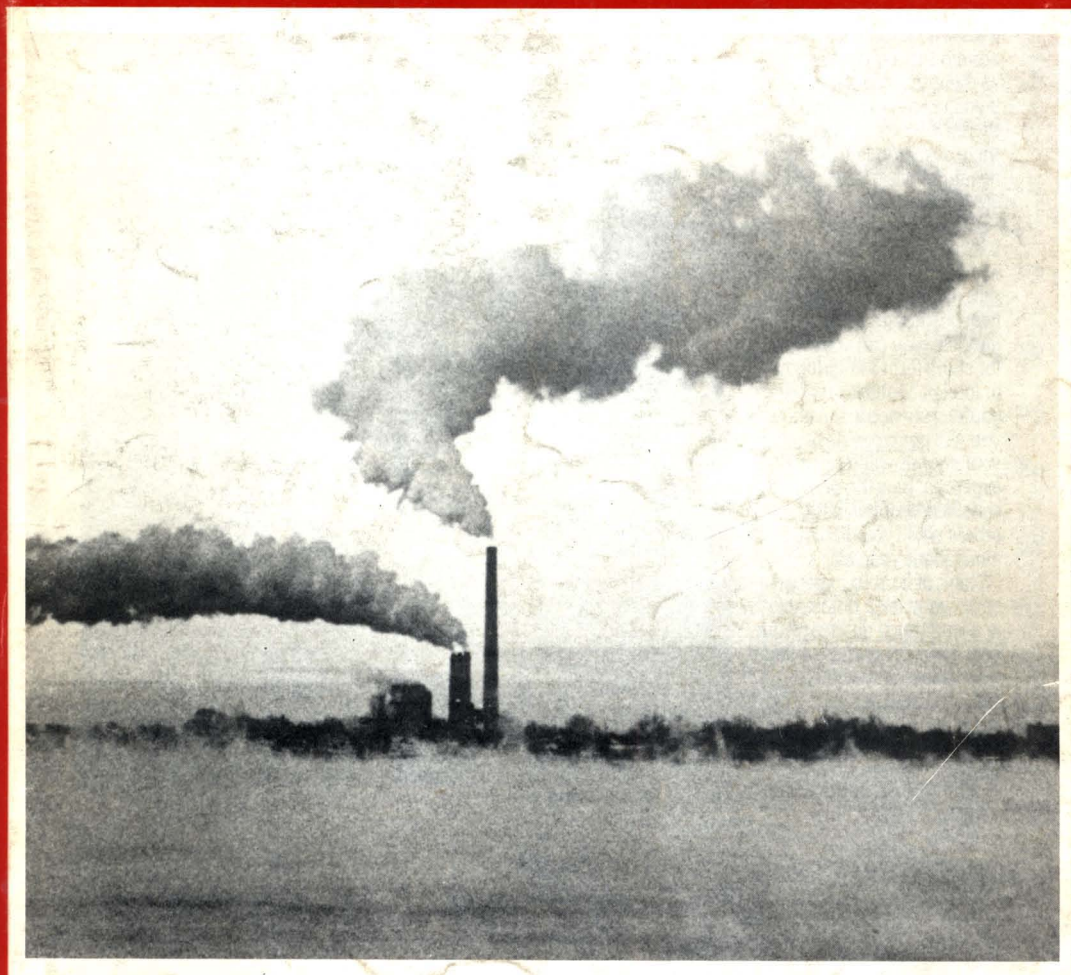# ENVIRONMENTAL PROGRESS

Condensation plumes show complex thermal structure and wind shear over Beverly-Salem (Massachusetts) Harbor. Photo by Ralph Turcotte, Courtesy of ENSR Consulting and Engineering, Acton, Massachusetts.

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ENVIRONMENTAL PROGRESS

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Europe and the Environment

By
Robert M. Bell and John F. Stevens

The environment, national environmental policy and international debate about the environment in Europe are all dominated by the European Community (EC), which is currently nearing the end of its fourth Action Program on the Environment. Indeed EC environmental legislation is now so extensive that is impossible to fully understand the national legislation of any EC member state without an understanding of the framework of the EC law within which the national legislation has to fit.

The history of this domination has been rather sudden. Before 1972, the EC had no environmental policy and the word "environment" was not even mentioned in the Treaty of Rome which was signed in 1957, and which essentially formed the EC. Now the 12 member countries have adopted over 200 items of EC environmental legislation whose aim has primarily been to "even out" or "make uniform" views over what are essentially disparate countries. As European history tells you in simple terms, many of the EC members states are probably more used to fighting one another than agreeing with one another.

As one may expect, this standardization has not been easy and horse trading and compromise is commonplace. Even so member states with well developed environmental policies have been made to amend their own policies to accommodate EC legislation. This has happened to those "environmentally aware" countries such as the Netherlands and the Federal Republic of Germany as well as those traditionally seen as "stonewallers" such as the United Kingdom.

EC environmental legislation has had effects in seven main areas:

WATER—where legislation has been orientated towards water quality standards for certain uses, and emission standards for discharges of dangerous substances.

WASTES—where directives deal with toxic wastes, transfrontier shipments, disposal of PCBs. Everyone is currently waiting for the draft directive of landfilling which once proposed stopping the UK traditional practice of the co-disposal of hazardous waste and domestic refuse.

AIR—where there are standards for products (vehicles and fuels), air quality standards and emission standards. The acid rain directive is probably the most important here, and proposed that member states reduce sulfur dioxide emissions by 60% by the year 1995. Compromise on this has caused a slippage of 2% and eight years from the original proposals.

CHEMICALS—where a directive restricts the marketing and use of dangerous substances.

WILDLIFE—where legislation restricts trading in endangered species, protects wild birds, and identifies special protection areas for wildlife.

NOISE—where more directives set noise levels for products (aircraft, cars, etc.).

ASSESSMENT and INFORMATION—where directives cover the need for environmental assessments for major products and in due course for compulsory auditing of large manufacturing plants.

The future for the environment in Europe appears equally to rest with the EC. The Single European Act of 1986 sets a target date of 1992 for the completion of the internal European market and actually gives more power to the EC in developing and implementing environmental policy. The lack of authority for environmental policy from the Treaty of Rome is made good and "environmental protection requirements shall be a component of the Communities other policies." It has been suggested that this enormously strengthens the hand of officials dealing with the environment when dealing with colleagues responsible for other policies.

There is absolutely no doubt that the environment is well and truly on the political agenda throughout Europe. Whether we Europeans are willing to put our money where our mouths are, and attempt to clean up some 200 years of environmental abuse is the questions on the minds of most.

Robert M. Bell is Managing Director and John F. Stevens is Senior Environmental Officer of the Environmental Advisory Unit of Liverpool University Limited, an environmental consulting firm headquartered in Liverpool, United Kingdom.

ห้องสมุดกรมวิทยาศาสตร์บริการ

DIPPR Starts Up Two New Projects in Environment, Safety, and Health

During 1990 and early 1991, AIChE's Design Institute for Physical Property Data (DIPPR) supported a project at Syracuse Research Corporation under Gloria Sage and Phil Howard. Funding was from the U.S. Department of Agriculture. This Scoping Study for Environmental Chemical Data Compilation—Project 891 developed the background guidance for DIPPR projects in environment, safety, and health. The study produced a list of high priority chemicals, properties and parameters to be considered, sources of data, and funding levels for segments of work.

Out of this work, the scope of Project 911 was drawn up. This project, Environment, Safety, and Health Data Compilation is to respond to a need for a crically evaluated, internally consistent, documented and computerized database covering environment, safety, and health properties for a select list of pure chemicals with known hazards. The project, similar in format to Project 801 on data compilation for the most common process industry chemicals, will satisfy industry and regulatory needs for more accurate and complete property data. The project's scope was developed around the 189 chemicals in the Clean Air Act list. There are six blocks of properties covering specific areas of interest. These are: oxygen demand parameters; partitioning parameters; general physical properties; vapor-liquid equilibria; fire and explosion; and sensory, health, and toxicity.

In August, requests for proposals were sent out to prospective contractors. From responses, the selection of Michigan Technological University in Houghton, Michigan was made. Co-principal investigators with the department of chemical engineering are Michael E. Mullins and Tony N. Rogers.

The second project identified as Environment Safety and Health Data Prediction Manual—Project 912 is to develop, evaluate, and recommend new and improved estimation methods useful in determining environment, safety and health behavior of chemicals.

Project 912 is the analog to the Data Prediction Manual—Project 802 which produced a data prediction manual for the chemical properties of interest in process design work. The same six blocks of properties described above for Project 911 will be covered in this project.

In response to requests for proposals sent out in March, 1991, the contract was awarded to Michigan Technological University with co-principal investigators Mike Mullins and Tony Rogers. Work on this project has been under way since May.

Since both projects are being conducted by the same staff, there will be a strong synergy between the two. Estimation methods developed in Project 912, based on data gathered in Project 911, will allow 911 to fill gaps in the database where no published data are available.

The projects are planned to be multi-year in length with funding to be set for each year and balloted through the DIPPR financing mechanism. Funding levels for 1991 and 1992 have been substantial, showing strong interest by the 15 companies supporting the work.

Those interested in details of the projects, who wish to become members should contact Marilyn Williams at the Design Institute for Physical Property Data, AIChE, 345 East 47th Street, New York, NY 10017; 212/705-7332.

Remedial Action Technology Demonstrated on ORNL Waste

A new technology being developed by the Department of Energy's (DOE) Office of Technology Development for conversion of old radioactive waste sites into glass by melting the contents of the burial pits and trenches was demonstrated on actual radioactive material at DOE's Oak Ridge National Laboratory (ORNL) last May.

Called *in situ* vitrification, the technique uses electricity to melt waste burial sites at very high temperatures, up to 1,500 degrees Celsius. When the molten mass cools, it forms a glass similar to the volcanic glass called obsidian. Sealed inside this glass, the radioactive material is immobilized so that it cannot escape into the surrounding earth or be carried away by water. The technique was developed at DOE's Battelle Pacific Northwest Laboratory (PNL).

In the demonstration, conducted jointly by ORNL and PNL through the DOE Office of Technology Development, a 12 metric-ton block of glass was produced in a simulated seepage pit containing a sample of sludge from an actual ORNL seepage pit. The sludge contained a small amount of radioactive cesium-137 and strontium-90. A maximum of 500 kilowatts of electricity was applied to the simulated seepage pit through four graphite electrodes for approximately 130 hours, melting the pit to a depth of nine feet. A large hood was placed over the simulated pit to collect any gases and particles released during melting. No radioactive material escaped from the containment system during the test. Melting was confined to the vicinity of the electrodes. The shape of the glass block formed is estimated to be a cylinder approximately seven feet in diameter and four feet in height, sitting on the ground nine feet beneath the surface.

A specially designed filter assembly was tested for its ability to capture all the radioactive particles released from the melt during op-

Brian Spalding, Oak Ridge National Laboratory (ORNL), Tennessee project officer for a test using electricity to melt buried waste, directs visitors' attention to the demonstration area. The test technique, known as *in situ* vitrification, converts old radioactive waste sites into glass by melting the contents of burial pits and trenches.

erations. Results suggest that the filter captured more than 99.99 percent of the small amount of radioactivity released from the melt to the off-gas. The majority of the radioactive material is retained in the glass, which is highly resistant to leaching by groundwater. This technique will be beneficial in reducing radiation exposures of workers during melting at actual contaminated sites.

After the glass cools, which will take several weeks, core samples will be taken to obtain specimens for determination of the material's composition and resistance to leaching by groundwater.

The demonstration was designed to test both the radiological safety of the vitrification process and a newly developed electrode feeding system where the graphite electrodes are allowed to slide into the melting material. The previous system involved placing electrodes deep in the ground before the electricity was applied, which would have required the hazardous operation of digging into contaminated waste.

Another research goal of the demonstration was to test a variety of nondestructive techniques for monitoring the shape and temperature of the molten material. These included seismic imaging, or the computer manipulation of transmitted sound waves to construct an "image" of the melt as it grows. This portion of the test was conducted jointly by researchers at the University of Tennessee and ORNL and was funded through DOE's Office of Basic Energy Sciences.

If demonstrations are successful, the technology may be used to provide permanent entombment for some 800,000 curies of strontium-90 and cesium-137 placed in seven trenches at ORNL between 1951 and 1966.

Those trenches are excavations into the native soil about 100 feet long, 15 feet deep and 3 to 6 feet wide. They were filled with limestone gravel to provide an open permeable material for the disposal of 42 million gallons of liquid radioactive waste.

Washington Environmental Newsletter

RCRA Reauthorization Initiatives

As expected, Congress has recently begun to seriously consider the reauthorization of the Resource Conservation and Recovery Act. General oversight hearings have already been held on various RCRA-related matters such as issues pertaining to municipal solid waste, recycling and packaging standards and interstate waste transport issues. Hearings are expected to continue throughout this year, focusing on the regulation of industrial wastes, hazardous secondary materials, toxics use and source reduction requirements, among others.

Several key Congressional environmental policy makers have proposed RCRA legislative initiatives that will most likely provide an initial framework for a comprehensive reauthorization bill. Senator Max Baucus (D. Mont.), Chairman of the Senate Subcommittee on Environmental Protection, has again proposed a reauthorization bill (S. 976), which, while focusing mainly on solid waste management requirements, also addresses certain hazardous waste issues, including toxic use and source reduction, S. 976, the *Resource Conservation and Recovery Act Amendments of 1991*, would impose significant new regulatory requirements on how solid and hazardous wastes are handled and managed. More importantly, this bill would, for the first time in the history of environmental regulation, impose *upstream* process-specific requirements on how industry actually manufactures products rather than just regulate end-point discharges.

Besides S. 976, there are several other RCRA-related proposals. Senator Chafee (R-RI) has introduced (S. 982) a bill specifically aimed at regulating hazardous waste recycling activities. While similar in concept to the Baucus bill, S. 982, however, would impose more stringent requirements on recycling of hazardous wastes. Chafee is concerned that hazardous wastes have been recycled without adequate controls in the past and there is a need to "gain control over this activity."

On the House side, attention has focused on Representative Al Swift's (D-WA) soon to be introduced RCRA proposal. Following the House's legislative approach during the 1990 Clean Air Act legislative deliberations, Rep. Swift, the Chairman of the House Subcommittee on Transportation and Hazardous Materials, has indicated that he will attempt to develop a consensus RCRA reauthorization bill over the next few months, with formal introduction this fall. This bill will focus primarily on solid waste issues, but some House members feel that since this issue was substantially amended in 1984, the issue should *not* be reconsidered since there are many regulations that still have not been issued under existing law.

Another area that will trigger debate relates to the issue of whether industry should be required, by statute, to implement toxic use and source reduction measures. Several environmental groups are urging Congress to shift its attention in RCRA from end-to-the-stream disposal requirements to up-stream pollution prevention requirements. According to these groups, these requirements are needed to complement the additional new pollution prevention reporting requirements that were passed as part of The Pollution Prevention Act of 1991. Under that Act, each owner/operator of a facility which is required to submit an annual toxic chemical release form under section 313 of the Emergency Planning and Community Right-to-Know Act of 1986, must include a toxic chemical source reduction and recycling report with each form submitted for the 1991 reporting year.

Overall, we expect that many of the proposed RCRA revisions (too numerous to outline here) will raise highly-contentious issues, and final reauthorization may not occur until after next year's elections.

A "Section by Section Summary" of S. 976 is available from AIChE's Washington Office.

ห้องสมุดกรมวิทยาศาสตร์บริการ

Controlling Volatile Emissions at Hazardous Waste Sites, Pollution Technology Review No. 126, John R. Ehrenfeld, Joo Hooi Ong, William Farino, Peter Spawn, Michael Jasinski, Brian Murphy, Douglas Dixon, and Edwin Rissmann, Noyes Data Corporation, Park Ridge, NJ, (1986), 412 pages, [ISBN No.: 0-8155-1063-2], U.S. List Price: $54.00

This book is divided into three parts. Each part involves an U.S. EPA sponsored study dealing with volatile organic emissions from treatment, storage, and disposal facilities (TSDF). These emissions are classified as being hazardous under the Resource Conservation and Recovery Act (RCRA). The emphasis is on landfills, landfarming, surface impoundments, and tanks.

Part A was prepared by John R. Ehrenfeld and Joo Hooi Ong of Arthur D. Little, Inc. Emission control technologies are discussed with efficiencies and costs identified. Surface impoundments, tanks, landfills, and landfarming are discussed in separate sections. Sufficient details are provided for making decisions on alternate control strategies.

Part B was prepared by William Farino, Peter Spawn, Michael Jasinski, and Brian Murphy of GCA Corporation and is a compilation of air emission release rate (AERR) models for volatile organic compounds (VOCs) from TSDFs. In addition to the four emphasis areas, VOC emissions are discussed for treatment units and drum handling and storage. Particulate emissions from waste piles are also discussed. The lack of pertinent data is a serious restriction of the models. Although for estimating purposes, each area discussed has a model that gives satisfactory results.

Part C is a compilation of the physical-chemical properties and categorization of RCRA wastes that was prepared by Douglas Dixon and Edwin Rissmann of Versar, Incorporated. The data are compound specific. The data are extracted from readily available sources. Many of the entries were estimated with methods found in the Handbook of Chemical Property Estimation Methods (Lyman et al., 1982).

By combining the three U.S. EPA reports into one source, this book provides a comprehensive treatment of VOC emissions from hazardous waste treatment facilities. Parts A and B are excellent treatments of the information available in 1984. Part C is a very convenient compilation of physical-chemical data; much of what is needed in the AERR models. The one strong negative that I found with the book was the poor print quality. Parts of the letters did not print, making the reading, for me, somewhat tiring.

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Water Distribution Systems: Simulation and Sizing, Thomas M. Walski, Johannes Gessler, and John W. Sjostrom, Lewis Publishers, Inc., Chelsea, MI, (1990), 321 pages, [ISBM No.: 0-87371-233-1], U.S. List Price: $82.00

In recent years, computer modeling has proved to be a reliable tool for solving problems related to water distribution systems. This book describes the capabilities of computer models and their use in analyzing these systems. The discussion proceeds from a general perspective applicable to an understanding of any of the computer programs popularly used to model water distribution systems to specific detail regarding the model developed by the authors. A copy of this model, WADISO (Water Distribution Simulation and Optimization computer software) is provided with the book.

The authors' expertise in the planning, design, operation, and modeling of water distribution systems is obvious throughout the book. Relevant rules-of-thumb are presented whenever helpful. The applications of computer modeling to the problems of water distribution systems are clearly and realistically detailed. The different modeling capabilities and requirements of smaller utilities are described and accounted for. The authors are certainly not "model happy" advocates of simulation for simulation's sake, but instead present a balanced view of the benefits of computer modeling.

The book is divided into three sections. The first section gives a broad description of the principles of modeling water distribution systems. The discussion follows the chronological order of the modeling process, from selection of a specific model through application of the model to problems of interest. Chapter topics include model selection and entry of system data, development of water consumption data, model calibration, problem solving, and pipe sizing with the final model. Missing from this section, though it would prove helpful, is a listing of available models and their capabilities and limitations. The chapter describing the types of problems a computer model can be used to solve is excellent and should motivate anyone involved with water distribution systems to consider computer modeling. This section of the book should prove valuable to anyone interested in applying computer models to water distribution systems.

The second section of the book introduces the basic ideas and methods of computer analysis of pipe networks and describes their incorporation in the WADISO model. Historically, investigators have favored the use of loop equations to analyze pipe networks. The authors provide a valuable comparison of the loop and node methods and although they clearly favor the node approach (having selected it for the WADISO model), their description of both methods is thorough and fair. Other considerations, such as the use of the Hazen-Williams or Darcy-Weisbach equation for friction losses, are also described. Chapter topics include the general pipe network problem, the loop and node methods used to solve this problem, the node method as it is used in the WADISO model, convergence characteristics of this model, and opti-

mization and simulation of networks with the WADISO model. This section shifts the emphasis of the book from a general overview of computer modeling to the WADISO model.

The final section of the book is the user's guide to the WADISO software developed by the authors for the IBM PC or compatible computers. Originally developed as part of the Methodology for Areawide Planning Studies (MAPS) of the U.S. Army Corps of Engineers Water Supply and Conservation Program, the software is now a stand-alone public domain program. A copy of this software (both source and executable code) on two 5 1/4-inch floppy disks is provided with the book. The source code is written in FORTRAN and accepts input in upper case letters only. The elegance of the program's input and output screens is limited by FORTRAN graphics capabilities, however, file input is allowed. Another nice feature is that during lengthy periods of operation, the program updates the user regarding job status. The program is a non-math coprocessor version, but you can recompile the source code to make use of a coprocessor if one is available. WADISO requires 586K of free memory space in order to run the program. This can be a problem with some versions of DOS on 640K machines. Chapter topics in this section include descriptions of the program control of the simulation, distribution, and extended period of time simulation routines and applications of these routines. The software itself has an extensive list of error messages most of which are self-explanatory. The manual, however, provides a valuable listing and explanation of each of these messages. Over 200 pages in length, this is the most extensive portion of the book. The excellent quality of this document certainly adds to the appeal of the WADISO model.

The WADISO software is really a three-part package composed of steady-state simulation, optimization, and extended time period simulation routines. The steady-state simulation routine makes use of the node and Hazen-Williams equations to solve for pressures and flows throughout a specified network. The optimization routine can be used to determine the economically optimal sizes of pipes in a system given specific pressure requirements and up to five loading patterns. Instead of using a mathematical optimization technique, WADISO enumerates every possible combination of pipe sizes and the associated costs to determine the optimal solution. The number of possible combinations is reduced by limiting pipe sizes to a set of commercially available sizes input by the user and by grouping together pipes whose size equality should be maintained. Because of the computing time required by this approach, the program is not intended to be used to size all pipes in a large network. The program, however, works quite well for problems encountered during expansion or reinforcement of existing systems where the sizing of a limited number of pipes is required. The extended time period simulation routine calculates pressures and flows in the network in the presence of time varying supply and demand functions. Applications of this routine include evaluation of pumping strategies, increased storage, pump replacement, and performance during emergency conditions. Although this is the most tedious routine in terms of data entry and output evaluation, it is also the most powerful.

I found the first two sections of the book to be quite readable, a characteristic not always found in a technical book. The final section is a detailed manual for the WADISO software. In keeping with old habits, I began to play with the software long before I had familiarized myself with the manual but found the manual a valuable reference. The index of this book is thorough, a feature I appreciate greatly in a reference book. The references regarding basic hydraulics and water distribution system analysis are good. However, I would prefer that the book reference some of the other software packages available for pipe network analysis and optimization.

In summary, whether you choose to use the WADISO software or not, this book is a valuable source of information about modeling water distribution systems. Engineers with interests from complete, in-house development of computer models to assembling data necessary to contract out modeling tasks will find this book to be a helpful reference.

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Screening and Utility Programs for Air Modeling

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Environmental professionals working on air pollution problems may be required to get an idea of the impact of a source before proceeding for a detailed analysis. Screening models available from the United States Environmental Protection Agency (EPA) can help in the work. The EPA modeling guideline [1] indicates that a screening analysis should be conducted to determine the maximum impact of a source. The screening results generally tend to overestimate the real life concentrations because of the assumptions used during modeling.

EPA also provides a number of utility programs making it easier to work with the data. This paper presents a brief description of the screening and utility programs available from the EPA. A list of the programs is given in Table 1. Most of the programs can be executed on an IBM PC compatible. The procedure for downloading the programs from the EPA Bulletin Board is given in the earlier review paper by Kumar and Mohan [2]. These programs are available free of charge.

SCREENING PROGRAMS

COMPLEX I is a second-level screening technique for evaluating the impact of sources in a rural complex terrain. The size of the source code is approximately 266 Kbytes. In order to prepare an executable file to run the program, you need to compile and link the subroutines of the source code using two utility programs. Some effort is required to prepare an input meteorological data file. The output can be directed to a terminal screen, a disk file, or a printer.

Table 1 List of Screening and Utility Programs Available from EPA Bulletin Board

(A)	Screening Programs	
	COMPLEX I	SCREEN
	CTSCREEN	SHORTZ
	LONGZ	TSCREEN
	PTPLU-2	VALLEY
	RTDM 3.2	VISCREEN
	RVD2	
(B)	Utility Programs	
	CALMPRO	PCRAMMET
	CHAVG	PREPFILE
	CONCOR	STAR
	MPRM	WINDROSE

The CTSCREEN model is a screening version of the Complex Terrain Dispersion Model CTDMPLUS. The model provides estimates of maximum 1-hour, 3-hour, 24-hour and annual concentrations. The program uses an array of predetermined meteorological conditions to model the information given in terrain and receptor files. These files can be generated using the preprocessor programs. CTSCREEN may be used in place of VALLEY, COMPLEX I and RTDM.

LONGZ is a second-level screening model for regulatory applications in urbanized complex terrain situations. The program is designed to calculate ground level seasonal and annual concentration from up to 14,000 sources. The program uses statistical wind summaries to calculate long-term average concentrations. The model can be applied to both flat and complex terrain and requires random-access mass storage capability.

PTPLU-2 is a first-level screening model used for use in a simple urban or rural terrain and is being replaced by the SCREEN model (discussed later on). The model is used to compute 1-hour ground level concentrations from a point source. The program allows for wind profile exponents, buoyancy induced dispersion, stack downwash, and gradual plume rise. The model output provides concentration as a function of wind speed and stability class. The results are given for both wind speeds constant with height and wind speeds increasing with height.

RTDM 3.2 is a third-level screening model used for evaluating the impact of sources in rural, complex terrain areas. The model is designed for chemically stable pollutants and is best suited for the study of buoyant plume impacts on receptors in terrain above stack top within about 15 km from the source(s). (A pre-processing program is included for preparing meteorological input data. A post-processing program is used for analyzing the model results.)

RVD2 is provided as a general service by the EPA. This is screening model to estimate plume rise, plume touchdown distance and concentrations for short term denser-than-air gas releases from vertical stacks or relief valve discharges. The concentrations are computed at plume touchdown and at up to 30 downwind distances specified by the user.

SCREEN model is based on the revised screening procedures document [3]. This model will replace the PTPLU-2 model described above. The program can handle point sources, flares and simple area sources. Building downwash, fumigation and complex terrain screening calculations are included in the program. The effects of terrain below stack height on the ground level concentration can be included for simple terrain screening. The program accepts user-specified distances.

SHORTZ is a second-level screening model for urbanized complex terrain situations. The program is designed to compute ground level gaseous or particulate concentrations from multiple sources. The averaging time for concentration ranges from 1 hour to 1 year. The program utilizes random access mass storage.

TSCREEN is a screening program to analyze toxic emissions using the SCREEN, RVD and PUFF dispersion models. A front-end control program directs the use of appropriate dispersion models with the help of interactive menus and data entry screens. The program occupies 1 MB of disk space. The input data for each scenario are saved to a file for future use.

VALLEY is a first-level screening model for rural complex terrain situations. The ground level concentrations are calculated using frequency tables for six stabilities, 16 wind directions and six wind speeds. Plume height is adjusted according to terrain elevations and stability classes.

VISCREEN is designed to calculate visual effects parameters for a plume as observed from a given vantage point. The program is a conservative screening tool for emission sources of particulate, NO, NO_2, and soot. The visual effects parameters delta E and contrast are calculated using three wave lengths of light (0.4, 0.55, and 0.7 μm) and for backgrounds against sky and dark terrain.

UTILITY PROGRAMS

The CALMPRO program reads meteorological data and concentration data from the files used for certain refined models. The influence of calm conditions is eliminated by zeroing hourly concentrations at all receptors. The program prepares an output of annual averages and high five 1, 3, 8 and 24 hour average concentrations.

CHAVG is a postprocessor program designed to read hourly concentrations from a disk/tape file and to compute running averages (averages that begin each hour and overlap) and end-to-end averages (averages that do not overlap) for four or five averaging periods. Averages are ranked for each receptor. The program output is generated for each averaging period for each type of average selected.

CONCOR is a useful program for converting UTM coordinates to latitude/longitude and vice versa. The program can be used as a subroutine in your FORTRAN program. The input for the program can be either a screen input or a file input.

MPRM program is a three stage system for processing meteorological data for use with the EPA dispersion models. During stage 1 you are required to identify files containing hourly surface data and upper air observations (and/or twice-daily mixing height estimates). These files are combined during stage 2 and a meteorological data file is created for your use in stage 3.

PCRAMMET program is a personal computer version of the RAMMET program. The results from the PCRAMMET program and RAMMET program are the same. The program processes hourly surface meteorological data (ceiling height, wind speed, wind direction, dry bulb temperature and opaque cloud cover) to determine atmospheric stability class for each hour and interpolates between twice-a-day mixing height data to compute a mixing height for each corresponding hour. The output is a binary file and can be used with models such as RAM, CRSTER and MPTER.

PREPFILE program reads the files created by RAMMET program and procedures these files in binary format on your computer.

STAR program produces a summary of the meteorological file by generating joint frequencies of six wind speeds, 16 wind directions and six atmospheric stability categories for the weather station and time period desired. The input file consists of hourly wind speed, wind direction, cloud height and total cloud cover. Output includes columns displaying the number of occurrences within each wind speed category for each wind direction and each atmospheric stability, respectively. The six wind speed categories are as follows: 1 to 3 mi/hr, 4 to 7 mi/hr, 8 to 12 mi/hr, 13 to 18 mi/hr, 19 to 24 mi/hr and greater than 24 mi/hr. The 16 wind directions are N, NNE, NE, ENE, E, ESE, SE, SSE, S, SSW, SW, WSW, W, WNW, NW and NNW. The program includes an option for air quality model selection. Current choices are CDM-2, ISCLT, LONGZ and VALLEY.

WINDROSE program is designed to calculate the information for preparing a windrose. The program computes the frequency of occurrence of wind direction with different wind speed categories. Two tables for frequency distribution are generated by the program. The first table is for the number of hours for each wind speed/wind direction category and the second table shows the percent frequency for each wind speed/ wind direction category. Data available from the EPA bulletin board may be used for running the program.

For the purpose of this review all the programs were downloaded from the EPA bulletin board by environmental engineering students at The University of Toledo taking courses on air quality modeling. All the screening programs include a test case and an introductory (READ.ME file) file. The screening programs and utility programs discussed above will occupy approximately 20 MB of disk space.

Note that the regulatory applications of air quality models are constantly changing. New guidelines are released on a regular basis. The readers are urged to contact regional EPA offices to find out current practices. It is hoped that you will find some time to try the above software for your applications.

LITERATURE CITED

1. U.S. EPA, "Guideline on Air Quality Models (Revised) and Supplement A (1987)," EPA-450/2-78-027R, U.S. EPA (1986).
2. Kumar, A., and S. Mohan, "Use of Bulletin Board System for Air Quality Modeling," Vol. 10, No. 1, pp. F8–F11, *Environmental Progress*, (1991).
3. U.S. EPA, "Screening Procedures for Estimating the Air Quality Impact of Stationary Sources," NTIS #PB89-159396, U.S. EPA, (1988).

Treatment of Contaminated Water, Air and Soil With UV Flashlamps

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A new and effective method has been developed for the treatment of VOC's, PCB's and other toxic organics. Direct UV photolysis of organics is achieved with this new method with the use of high intensity ultraviolet light of a broad UV spectrum. Standard and novel UV flashlamps can be used for generation of this broad UV spectrum. The pulsing nature of such spectrum helps to increase the efficiency of destruction of toxics. The final products of this destruction process are non-toxic simple compounds. The energy efficiency of this new process exceeds that of traditional UV aided processes with medium pressure mercury lamps. This article reviews the Direct UV Photolysis Process, gives experimental results, and provides recommendations for applications in the treatment of groundwater, wastewater, contaminated air and soil.

INTRODUCTION

Treatment of aqueous solutions containing toxic organics is of widespread concern in industry. Enormous quantities of groundwater are contaminated with volatile organic compounds (VOC's) such as trichlorethylene (TCE), benzene, toluene, xylene, etc. Additionally, many manufacturing facilities produce wastewater containing polynuecleoaromatics (PNA), PCB's etc., which, if not properly contained, contaminate surface water, air and/or soil. Established methods of toxic treatment have to be re-evaluated under increasingly restrictive regulations.

Ultraviolet technologies offer the advantage of being very effective when compared to other processes because the UV-aided process totally destroys the contaminants leaving no residue. Other traditional technologies, such as filtration of contaminated water or the use of air stripping towers simply transfer toxic contaminants from one environmental medium to another, e.g. from water to air. Each traditional UV technology has its advantages and limitations, reviewed in [1] and briefly described in two sections below as first and second generation UV systems.

First Generation UV Systems

The basis of these first generation UV technologies is the use of 254 nm light emitted by conventional mercury vapor lamps. This line generates active radicals from peroxide or from ozone which are added during treatment to contaminated water. Some established systems, such as those produced by Peroxidation Systems (PSI) and ULTROX, require that the peroxide or ozone be thoroughly mixed with the water being treated [1, 2, 3]. The mixture must also be kept under UV light until the oxidants are converted into free radicals, which subsequently destroy toxic organics. This is a conventional advanced oxidation process (AOP) which, for example, for destruction of TCE is known to be as follows:

$$\text{STEP 1:} \quad \left. \begin{array}{l} O_3 + UV \\ H_2O_2 + UV \\ H_2O_2 + O_3 + UV \\ H_2O_2 + M^+ + UV \end{array} \right\} \rightarrow \ ^\bullet OH$$

$$\text{STEP 2:} \quad TCE + \ ^\bullet OH \rightarrow 2CO_2 + 3CL \quad (1)$$

Where STEP 1 has one of 4 choices.
The traditional UV assisted process shown above has three drawbacks [1]:
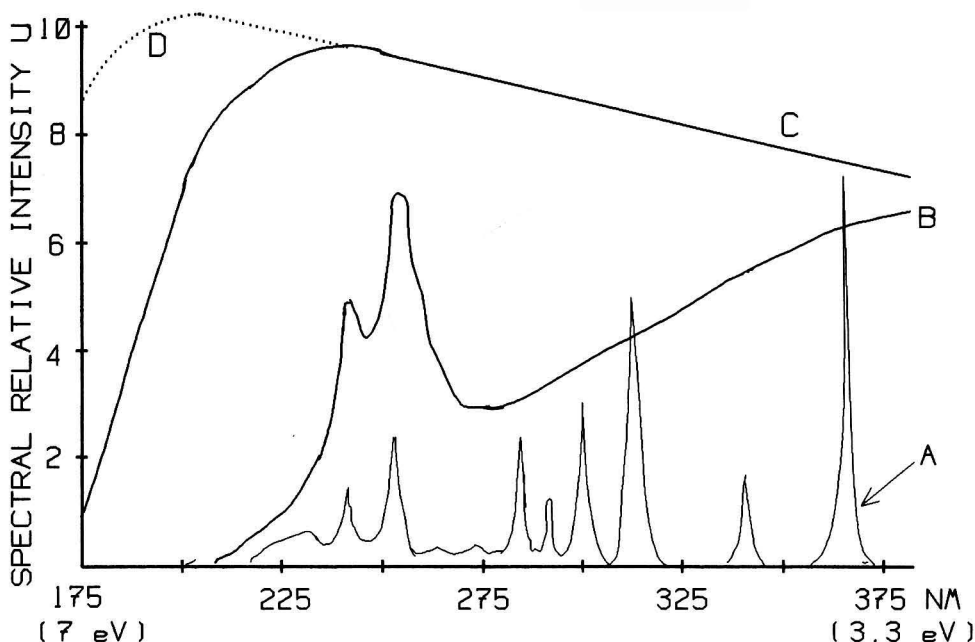
FIGURE 1. Spectral distributions in the region from 175 nm to 375 nm for four UV sources (A, B, C and D) in relative units U. Corresponding maximum and minimum photon energies for the region are given in eV (1 eV = 1.6 10^{-19} Joules, 1 nm = 10^{-9} m).

A. Medium pressure mercury lamp at the electrical load of 60 watt per lamp cm.

B. Xenon flashlamp, 450 Torr, arc length 5 cm, current density 8700 A/cm², bore diameter 4 mm, energy 45 Joules, pulse duration 125 μsec [9, part 2]. The UV output at these power conditions is close to the maximum one can get from a xenon flashlamp.

C. Optimal spectra of a UV pulsed lamp. This curve is a fair approximation of the output from the WEKHOF lamp [10] at 60 watts per lamp cm.

D. Black body radiation at the same conditions as C. This is the maximum radiation for a plasma temperature achieved during tests and contains photons with energies which are absorbed by quartz.

1) An excess of oxidants added in the treated stream can interfere with process flow or materials.

2) Reaction times in the processing chamber are prolonged, allowing for precipitates to form on the lamps and reduce the light supply.

3) These processes require large units.

Another drawback of such an approach is its limitation to contaminants in water. There are only limited data on its use for soils and air.

Second Generation UV Systems

UV photons are also capable of destroying organic toxics directly without the use of additive oxidants by breaking chemical bonds in organics through photodissociation. Such process requires photon energies from 4 eV to 7 eV (their wavelengths from 300 nm to 175 nm respectively, where 1 eV = $1.6 \cdot 10^{-19}$ Joules). For example, a direct UV photolysis of TCE is shown as follows:

$$
\begin{array}{cc}
\text{Cl} & \text{H} \\
| & | \\
\text{C} = \text{C} + \text{UV} \rightarrow 2\text{CO} + 3\text{Cl}^- \\
| & | \\
\text{Cl} & \text{Cl}
\end{array}
\qquad (2)
$$
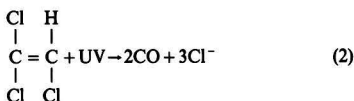
For dissociating to occur, the UV wavelength must match up with the absorption band of the target contaminants. An absorption band can be as narrow as 1 nm or as wide as 20 nm. Each toxic contaminant has an optimal wavelength for photodissociation where its effectiveness, described by the molar extinction coefficient ϵ, is the largest [4]. For example, benzene absorbs strongly at 184 nm ($\epsilon = 47,000$) and at 202 nm ($\epsilon = 7,000$) plus has series of weak absorption bands between 230 nm and 270 nm ($\epsilon \approx 300$). Acetone has absorption bands at 220 nm ($\epsilon = 16,000$) and 318 nm ($\epsilon = 30$), while TCE has a strong band around 230 nm.

If a complex organic undergoes photodissociation, it may have byproducts which can also be toxic while its absorption bands are most likely differ from ones of the original organic. For that reason a further photodissociation is necessary until only non-toxic byproducts are left. This condition, as well as a presence of many different toxics in media, requires a dense structure of UV emission lines to support effectively the direct photolysis.

There are very limited choices of UV line sources which can do this job effectively. In fact, first generation UV sources generate only a very few lines in the shortwave UV region, and the strongest is the 254 nm line from mercury vapor lamps [1, 5]. Traditional medium and high pressure mercury vapor lamps having input powers over 200 watt/inch [80 watt/cm]

generate few other lines including 248, 265, 280, 297 and 302 nm, Figure 1a. Thus even high power medium pressure mercury vapor lamps cannot break most chemical bonds directly due to the limited available wavelengths not matching absorption bands of the targeted organics.

The number of UV lines in the deep UV region can be somewhat increased with dopants like iodides and magnesium placed into medium or high pressure mercury lamps [5]. Such lamps are known as metal halide lamps. Dopants in such lamps can be selected to fill wavelength gaps between mercury lines. Systems which employ lamps with dopants (SOLARCHEM systems is the best example [6]) are more effective than the first generation UV systems [7]. These systems are able to treat organic toxics both with and without adding an oxidant, i.e. they destroy toxics either in accordance with reaction (1) or with (2) or both. Adding peroxide combined with the adding a photocatalyst to increase its efficiency helps to double the overall process efficiency of such systems. That is because UV lines which dissociate peroxide are different from UV lines which dissociate targeted organic toxics. Thus, when an oxidant is used, mercury lamps with dopants have more efficient use of UV energy as well as better oxidizing byproducts, which cannot be broken further due to the lack of necessary emission lines in the lamp spectra.

Wekhof Process—The Third Generation UV Systems

The use of dopants in UV lamps has its limitation for creating additional UV lines to match absorption bands of selected toxics. In fact, any UV lamp with line emission does not have a sufficient number of UV lines which will effectively support direct photolysis in a media where many toxic compounds are present.

The alternative to the lamp with a line emission is the source of the **UV continuum** which overlaps absorption bands of all toxics present. If the UV continuum has sufficient intensity it can destroy all organics in a medium through the direct photolysis (2). The process can achieve a complete disintegration of toxics into non-toxic byproducts. Byproducts can be oxidized since oxygen is usually dissolved in water and is abundant in both air and soil. In the case of water treatment a peroxide can be added to increase the process efficiency.

The following sections describe the process, experimental results and recommendations for applications in groundwater, wastewater, contaminated air and soil.

EXPERIMENTAL

Sources of UV continuum
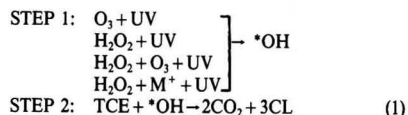
A broad UV spectrum similar to UV continuum and having a sufficient intensity can be generated by various pulsed devices [5]. Out of all such devices xenon and custom build flashlamps are the most simple and cost-effective for destruction of toxic organics. Standard xenon flashlamps generate a close to the required spectrum. Flashlamps are pulsed devices where xenon gas is converted to a plasma and heated by a short pulse of electric current. In order for a lamp to operate properly, one has to run it at nominal parameters where the lamp current density j and the pulse duration τ fall into ranges such as $1 kA/cm^2 < j > 5kA/cm^2$ and $150 \mu sec < \tau > 1$ msec. In this case, xenon plasma temperature ranges from $6,000°K$ to $9,000°K$ and emit from 5% to 8% of all radiation below 300 nm respectively [5, 8, 9].

A dramatic increase in UV output for all wavelengths below 300 nm occurs if a xenon flashlamp is operated under a severe stress with a current density j in the range from $6kA/cm^2$ to $14 kA/cm^2$ [8,9]. A corresponding spectrum (for $j = 8.8$ kA/cm^2) is presented on Figure 1b. However, such operating conditions shorten the life of the lamp (reduces the total number of flashes) by up to 100-fold or more. A trade-off can be achieved between the UV output, the lamp lifetime and operating costs for toxic treatment. The desirable and in principle achievable UV spectrum of a flashlamp is presented on Figure 1c [10].

Description of the test apparatus

The block diagram of the experimental apparatus is presented on Figure 2. In our initial tests, we used a standard xenon flashlamp with a bore diameter of 7 mm and with a discharge gap of 6 inches (15 cm). The lamp was loaded from a pulse forming network (PFN) where a capacitor C (5 or 10 μF) was charged to voltage of V = 3 kV and then discharged into the lamp through an electronic switch (silicon controlled rectifier, SCR). In later tests we used a custom designed UV flashlamp with a spectra similar to the one on Figure 1c [10].

Our circuit provided the rate of current rise dI/dt up to 300 A/μsec, peak currents I up to 3 kA and the current density from 6 kA/cm² to 12 kA/cm². Another capacitor C and a charging voltage V can be used to achieve the same current density as well. However, smaller peak currents and smaller dI/dt will result in a lesser UV output.

Treated water (or air) was moved through a quartz processing chamber (3 cm in diameter, 20 cm long) placed alongside the lamp. The UV flashlamp and the quartz processing chamber were encircled (optically coupled) by an elliptical UV reflector. The processing chamber was connected to a batch vessel (1.5 L) through forward and return lines, and a pump was placed on a forward line. The flow rate through the system could be adjusted. The system could also treat water or air flowing only through the processing chamber. In a number of tests, the lamp was placed along the vertical axis of a 6-L processing chamber made from a stainless steel. Samples were taken through a short drain line with a valve so that there was no exposure to the ambient air. All tests were taken and analyzed by an independent customer or a laboratory.
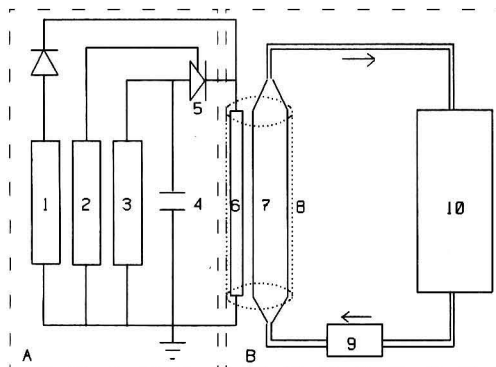
FIGURE 2. Experimental apparatus for a small scale testing at UVERG facilities.

A. Electrical diagram: (1)—simmer power supply (200 V, 3 A); (2)—control unit; (3)—capacitor charging power supply (2 kV to 5 kV); (4)—capacitor (5 μF to 100 μF); (5)—silicon controlled rectifier (SCR); (6)—xenon (or custom) UV flashlamp. When a medium pressure mercury vapor lamp was used, it had it's own power supply.

B. Water treatment unit: (7)—quartz processing chamber; (8)—UV elliptical reflector; (9)—pump; (10)—batch volume.
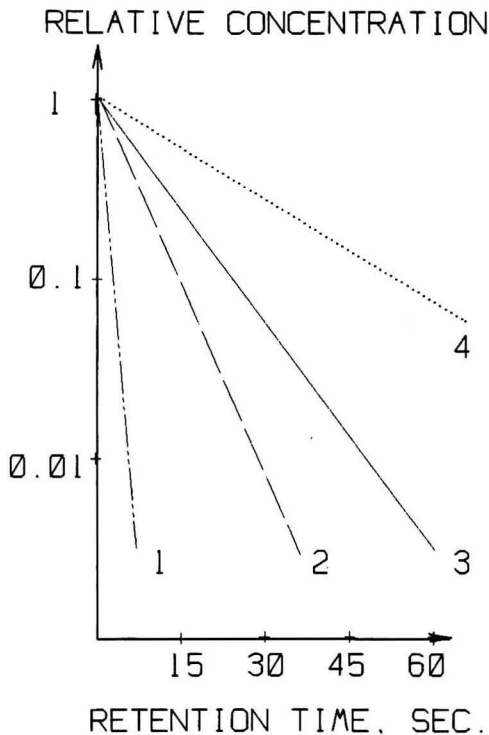
FIGURE 3. Retention times for toxics in media. Data obtained with UV from a 15 cm xenon flashlamp at the load of 60 watt per lamp cm; (1)—TCE in air; (2)—TCE in water; (3)—Benzene in water, Data obtained with 15 cm long medium pressure mercury vapor lamp at 60 watts/cm, peroxide was added: (4)—TCE in water.
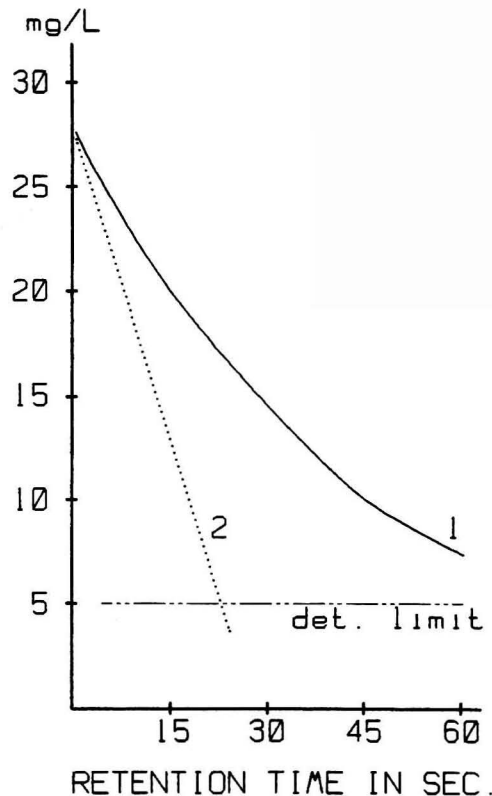
FIGURE 4. Retention times for reduction of saturated oil and grease in a field sample brought by a representative of Pacific Gas & Electric Company from a power plant at Hunters Point, San Francisco, CA. The same test conditions as for Fig. 3: (1)—medium pressure mercury lamp; (2)—pulsed xenon flashlamp.

Tests with water

We compared the effectiveness of direct photolysis supported by a xenon flashlamp and the traditional UV/oxidation process with peroxide supported by the 254 nm UV line from a medium pressure mercury lamp. The electrical consumption was the same for both lamps and equal 100 and 150 watts per lamp inch [40 and 60 watt/cm]. For some of these tests, tap water was spiked with different compounds (one for each series of tests) and some tests were done with real waste water or with site groundwater. A qualified third party provided either spiked samples or field samples and their analysis. The following toxins were treated in our tests: TCA, TCE, benzene, PNA, saturated oil and grease also bacteria and others. In some tests we added peroxide to the treated water. Some of the results of these tests are presented in Figures 3, 4, 5, and 6.

As can be seen from Figures 3 and 4, the effectiveness of direct photolysis achieved for TCE and for saturated oil and grease exceeds up to a few times the traditional Advanced Oxidation Process (AOP). The process has an impressive effect on bacteria (Figure 5): each UV pulse decreased a population of bacteria in water about 100 times. The results with bacteria were later confirmed by Maxwell Laboratories, Inc., San Diego, CA.

Tests with air

We used the same apparatus for tests in which air was spiked with TCE or with benzene vapors and then passed through the processing chamber. There was no recycle for the air. Our preliminary data showed that the organics destruction in a gas flow was about five times faster than in water, Figure 3.

Soil tests

We performed these tests on soil spiked with approximately 800 mg/kg of PCB's, 650 mg/kg of DDT and 550 mg/kg PNA's. Since UV does not penetrate the soil matrix, one has to use a surfactant to extract the contaminants from within the soil up to its surface and then to rake the solids continually. We used a standard surfactant, Sodium Lauryl Sulfate ($C_{12}H_{25}O_4SNa$) in 1% solution. It was sprayed at the rate of about 0.5 g/cm² min while raking the soil every 2 minutes. Sample sizes were 200 g and were placed in a shallow and wide container (2 cm × 7 cm × 18 cm). The distance between soil and a flashlamp was 5 cm. The flashlamp had a parabolic UV reflector for a uniform distribution of UV light over the soil sample.

Two series of soil tests were performed: one with a 15 cm long flashlamp and another one with a 15 cm long medium pressure mercury lamp. In each case, the lamps had the same power consumption of 60 watt per lamp cm. We found that the pulsed UV lamp was much more effective than a medium-
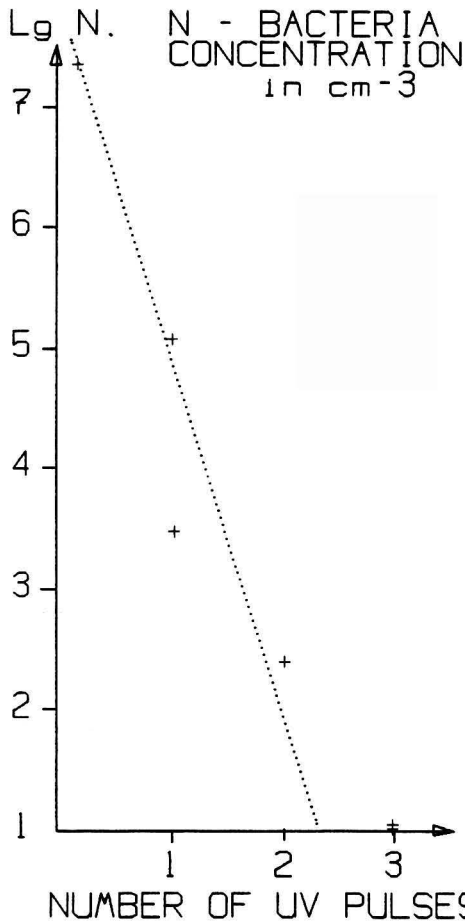
FIGURE 5. Disinfection test with a pulsed Xenon flash-lamp. Pulse energy 20 Joules, Water volume 1 L with injected E-coli bacteria.

FIGURE 6. Retention times for PNA compounds de-stroyed with pulsing UV from a 15 cm xenon lamp at 60 watts/cm: (1)—Perene; (2)—Acenaphthene; (3)—Naph-thaline; (4)—Fluorine.

pressure lamp for destruction of chemicals in soil. The 30-min. exposure from a pulsed lamp reduced PCB, DDT and PNA concentrations by 85 +/− 5% (Fig. 7). On the other hand, the presence of chlorine compounds in the soil did not increase.

Data Analysis

In various tests the following organic toxics were disinte-grated with a pulsing UV continuum (Wekhof Process):
1. Petroleum Compounds such as benzene, gasoline, tol-uene, MTBE, oil and grease, etc.
2. Polynuclear Aromatics such as naphthalene, perene, etc.
3. Double-bonded organics such as TCE, etc.
4. Saturated organics such as TCA, carbon tetrachloride, chloroform.
5. Pesticides such as DDT, DEE.
6. Cyanides.
7. PCB's, dioxins.
8. Nitrites and nitrates.
9. Pink water (TNT).
10. Bacteria.

The variety of organics disintegrated by a pulsing UV con-tinuum shows that the process has a universal application. The destruction efficiency depended on a type of the organic; for example, it was higher for TCE and xylene and lesser for benzene and TCA. In most cases of water treatment, except for TCE, the addition of peroxide increased the process ef-ficiency two or more times. The reason for that is the same as for the second generation UV systems—a better use of UV energy since peroxide absorb its own part of the UV spectra and toxic organics absorb different parts of the UV spectra.

The rate Γ of the photodissociation process can be simply calculated with the following correlation:

$$\Gamma = \Phi \cdot \sigma \cdot n [cm^{-3} sec^{-1}] \qquad (3)$$

where

Φ—UV flux within an absorption band (photons/cm$^2 \cdot$sec)
σ—cross-section for a photodissociation of an undesirable compound; a typical peak σ value is from 10^{-17} cm^2 to 10^{-16} cm^2 and has to be measured or calculated for each absorption band.
n—concentration of toxics per cm^3 of the carrier medium.

Our estimates showed that our lamps provided sufficient UV fluxes Φ within absorption bands, at least 0.1 watt/cm^2/ nm within the treated media. Thus, commercially acceptable rates of toxic destruction such as $\Gamma = 1$ mg/L/sec were achieved. Similar fluxes were generated in tests with mercury medium pressure lamps, but their few UV lines didn't have sufficient matching with absorption bands of treated toxins. That is one of the reasons for their poor performance comparatively with UV flashlamps of the same power.

The more effective action of the direct UV photolysis with pulsing UV vs. the 254 nm line + peroxide process (Figures 3 and 4) can be explained in terms of equation (3). Although both lamps consumed the same electrical power, the values of UV fluxes Φ emitted within absorption bands and respective
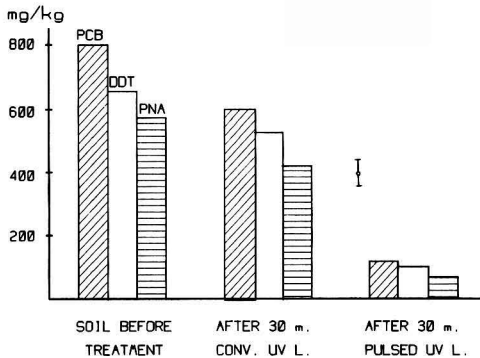
FIGURE 7. Reduction of PNA's, PCB's and DDT from the soil, placed into a 18 cm by 5 cm tray in 1.5 cm thick layer. The lamp was 5 cm from the soil and had a parabolic UV reflector. (1)—Initial concentrations. (2)—Reduction after 30-min. treatment with a medium pressure mercury lamp at 60wt/cm load. (3)—reduction after 30 min treatment with UV pulsed lamp at the same loading.

dissociation cross-sections σ were higher for the pulsed process than those for the UV flux of 254 nm line and σ for creating active radicals from peroxide [Equation (1)].

There is also another important advantage in using a pulsed UV source. It is its ability to produce very high photon fluxes, which are thousands of times higher than the same energy per second emitted continuously. This changes the kinetics of photochemistry in a way which speeds up targeted reactions. These higher photon fluxes have three distinct characteristics: peak power, RMS power and average power.

Peak power P(p) is defined as ratio between the energy of a single pulse $E(p)$ and a time duration τ of a pulse:

$$P(p) = E(p)/\tau. \tag{4}$$

The **RMS power P(rms)** defines the effectiveness of the periodically repeated pulsed action of the peak power $P(p)$ at the repetition rate **R**:

$$P(rms) = 0.5 \cdot P(p) \cdot \sqrt{\tau \cdot R} \tag{5}$$

Average power P(a) is the combined energy of all pulses delivered in 1 second at the repetition rate **R**:

$$P(a) = E(p) \cdot R \tag{6}$$

The peak power is thousands of times as much as the average power emitted (and consumed) by a pulsed lamp. We found [11] that with the same spectral interval of the UV source the effective destruction achieved by the process was attained when the ratio of rms power $P(rms)$ to average power $P(a)$ falls in the characteristic range of 1:10 to 1:100. The ratio of peak power $P(p)$ to average power $P(a)$ falls in the characteristic range of 1000:1 to 10,000:1; and the average power density is maintained at least at a value of about 0, 1 Watt/cm^2/nm within the treated medium.

Within these ranges, one has to determine experimentally the best ratio for the destruction of each particular toxic and its concentration, or for a combination of toxics. The ratio of RMS to average power does not have to be selected if the ratio of the peak to average power is found for particular toxics: it will be present within the specified range anyway.

The existence of effective power ratios for this process can be explained by the fact that the ratio of the peak power to the average power is indirectly related to the plasma temperature, and, by this, shifts the peak of UV generation to a region with targeted absorption bands.

A faster destruction of organics in air than in water can be explained by a combination of three factors:

1. Lower UV absorption by air than by water.
2. Higher mobility of dissociated species which prevents the reverse process of toxics recombination.
3. Presence of oxygen in the air, so that UV converts a small part of the oxygen into ozone which contributes to the UV-aided photolysis, [Equation (1)].

The presence of air also helped to oxidize byproducts in soil. This means that destruction of organics was followed by a full mineralization of the process byproducts and by their escape from the soil. This explains why there was no increase in chloride compounds in the treated soil.

Processing Costs and Engineering Recommendations

Estimates are made for wastewater containing 20 mg/L TCE plus 20 mg/L benzene. The target reduction was 100-fold for each compound. Two established methods of treatment such as air stripper with off-gas vapor phase carbon, based on data from Westates Carbon Inc., (Los Angeles, CA), and a conventional UV/peroxide method based on LV60 system from PSI (Tucson, Arizona) are compared with the treatment projected for 20 kW UVERG system. A detailed costs breakdown for each of three cases is presented in TABLE 1. The results show a considerable advantage for the Wekhof process.

Operational costs for soil treatment with Wekhof Process, (such as on Fig. 7), were estimated to be between $120/$m^3$ and $250/$m^3$. This treatment can be performed at the rate of 1 m^3 per 24 hours with a 100 kW system mounted on a trailer. For comparison, treatment of such grossly contaminated soil by bioremediation may take a few years at double the cost while treatment by incineration creates a strong air pollution and

TABLE 1. ECONOMIC COMPARISONS FOR GROUNDWATER TREATMENT SYSTEMS
projected at the following assumptions:

Contaminant: 20 mg/L benzene plus 20 mg/L TCE;
Target reduction: 100-fold each;
Flow rate: 100 gal/min (0.38 m^3/min);
Operating costs are given for 1 year roundclock operation.

I T E M	AIR/CARBON	PSI LV60	UVERG 20
EQUIPMENT	$ 100,000	$ 115,000	$ 115,000
INSTALLATION	20,000	20,000	15,000
CAPITAL COST	$ 120,000	$ 135,000	$ 120,000
EL. POWER	$ 5,120	$ 34,500	$ 11,400
CARBON COST	$ 274,300	$ 0	$ 0
CHEM. COST	$ 0	$ 12,000	$ 6,000
LAMPS COST	$ 0	$ 38,400	$ 17,800
MAINTENANCE	$ 15,600	$ 6,750	$ 6,000
AMORTIZATION	$ 24,000	$ 27,000	$ 25,000
TOTAL OPER. COSTS	$ 319,020	$ 118,650	$ 66,200
TREAT. COST $/$m^3$ ($/1,000 gal)	$ 1.60 ($ 6.07)	$ 0.59 ($ 2.24)	$ 0.33 ($ 1.26)

makes the cleaned soil useless for vegetation. The soil treated with pulsing UV retained its vegetation properties.

An environmental engineer should consider the following applications of this new technology:

1. **Groundwater treatment**
   a) Direct treatment providing that water is filtered from solid compounds and has no coloration.
   b) Water can be treated by air stripping towers where the pulsed UV process cleanse its exhaust.
2. **Wastewater treatment**
   a) The recycling of the wastewater at plants which use water for product washing.
   b) The recycling of water at power plants.
   c) Water regeneration at refineries.
3. **Air treatment**
   a) Emission control at plants.
   b) Bacteria' control in large air conditioning systems, i.e. hospitals.
4. **Soil remediation**
   a) Remediation firms may consider to acquiring transportable soil UV processing units to treat small amounts of highly contaminated soil on customer sites.
   b) Treatment of a soil which has to retain its vegetation properties.

CONCLUSIONS

Our data allows us to conclude that the direct photolysis with intense pulsing deep UV continuum (Wekhof Process) is both the most efficient and clean method of organics destruction in water, gas and in soil. Adding peroxide in wastewater will further increase the process efficiency.

The requirements on pulsing UV sources exceed that of other commercially available (however, a limited use of xenon flashlamps is possible). A new custom-built source—WEKHOF UV flashlamp is recommended.

Each group of organics has the most efficient destruction if UV continuum is delivered with specific ratios between peak and average powers providing that the average UV power within the targeted toxic absorption band equal at least $0.1 \text{ wt/cm}^2/\text{nm}$ in the bulk of the treated medium.

The standard oxidation process with peroxide plus 254 nm UV line from a medium pressure mercury lamp has at least a three-fold less efficiency than the process with a lamp generating a pulsing UV continuum and consuming the same electrical energy.

LITERATURE CITED

1. Kimberely Roy, "Series on UV/oxidation technologies," *Hazmat World*, **6**, n.6, n.7 and n.8 (1990).
2. Bradford H. Miller and Kirshna V. Mayenkar, Emcon Associates, "Optimizing Treatment Design by Performing Treatability Studies Comparing UV Systems," Hazmacon 1991, CA.
3. David A. Cheuvront, Christopher L. Giggy, Carl G. Loven and Geoffrey H. Swett, "Groundwater Treatment With Zero Air Emissions," *Environmental Progress*, **9**, 3 (1990).
4. John R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc. Englewood Cliffs, N.J. pp. 4–21, 1965.
5. Roger Phillips, "Sources and Applications of Ultraviolet Radiation," Academic Press, London (1983).
6. Keith Bircher, Solarchem Corp, Richmond Hill, Ontario. Private communications.
7. Solomon E. Layndres, John T. Rees, Edwin N. Folsom, Anthony J. Boegel, "Treatment of Ground Water Contaminated with Volatile Organic Compounds Using Second Generation UV Light Technology," Report on Hazmacon, San Jose, CA (1991).
8. "Applications of Xenon Flashlamps," Manual, EG&G Corp., Salem, MA (1990).
9. "Introduction to Flashlamps," Technical Bulletin 1, 2 and 3 by ILC Technology, Inc., Sunnyvale, CA (1989).
10. Alex Wekhof, "High Power Pulsed UV Source," Patent Application, filed Dec. 10, 1990.
11. Alex Wekhof, "Novel UV Process of Destruction of Organic Toxics in Media," Patent Application, Disclosed in June 1989, Filed June 28, 1990.

Limiting Emissions of the Greenhouse Gas, CO$_2$

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While considerable global warming uncertainties remain, limiting the emission of the greenhouse gas, CO$_2$, at minimum cost is a growing social concern. An approach suggested is to generate electricity by processes that facilitate capture of the CO$_2$, and then to compress and inject it into suitable underground formations. By using formations containing uneconomical deposits of energy sources such as oil, gas, Fe^{++}, coal, etc., underground bioconversion of the CO$_2$ to recoverable fuel forms may prove possible.

BACKGROUND

While concern about providing a sufficient and economic supply of energy continues and considerable global warming uncertainties remain, the concern about the effect of greenhouse gases on global temperatures has been growing. Hence, the fact that CO$_2$ is a significant contributor has cast a shadow on using fossil fuels to supply the increasing need for energy. The general routes by which to resolve the two needs that have been suggested include the use of fuels with a high hydrogen content, improving the efficiency of the use of the fuel, improving the efficiency of the conversion of the raw fuel to its marketable form, and disposal or reuse of the resultant CO$_2$. Since the first two of these routes are controlled by the fuel user, only the last two are at the disposal of the supplier.

Some work has been done on means of collection and disposal of CO$_2$. Studies of the collection, for example, by scrubbing, of the CO$_2$ emitted from the stacks of existing electric generating plants using coal-fired, air-blown boilers have concluded that the cost would be high—an increase in the cost of electricity of approximately 75% [1, 2].

As a result, studies at the University of Utrecht and a part of this study have concentrated on the process for the generation of electricity known as the Integrated Coal Gasification Combined Cycle (IGCC), which was tested at a 100 MW plant at Coolwater, CA [3]. In large measure, the results from the work at the University of Utrecht, which concerned the isolation and disposal of the resultant CO$_2$, paralleled those of this study [2]. By adding a water gas shift step to the basic oxygen-blown coal gasification process to convert the bulk of the CO in the raw gasifier product to CO$_2$ and hydrogen, it is possible to use conventional acid gas scrubbing units to separate the resultant CO$_2$ and obtain a product fuel gas made

up primarily of hydrogen whose combustion produces water vapor. The CO$_2$ may then be compressed and dehydrated and may be injected for disposal into abandoned oil or gas wells or into other porous underground formations. The estimated incremental cost of electricity is 30% based on preliminary design and cost estimates by architect engineers [4, 5] and incremental costing by the University of Utrecht [2].

In the present engineering study, four aspects of the problem have been analyzed. These are: a) separation and preparation of the CO$_2$ for disposal; b) injection of the CO$_2$ into porous underground formations; c) the selection and modification of electric generation processes for efficient CO$_2$ control and low cost of electricity; and d) the fixation and reuse of the CO$_2$ as a fuel.

ISOLATION OF THE CO$_2$

Since the earlier work showed that it was very expensive to separate the CO$_2$ from the stack gases of a plant in which a fossil fuel was combusted with air, all the process options examined in this study either used oxygen for combustion or conversion of the fossil fuel, or otherwise produced a stack or process gas largely free of nitrogen with most of the carbon as CO$_2$. As a result, in most cases, the primary step in readying the CO$_2$ for disposal involved its isolation by conventional acid-gas scrubbing of the CO$_2$, plus the SOx and NOx or their precursors if they are present.

Compression of the resultant CO$_2$ stream is necessary in order to inject it into an underground formation. CO$_2$ compression, typically to 2,000 psi, for deep-well injection is already commercial for enhanced oil recovery. It has been found that tiny concentrations of water in CO$_2$ injected into wells are corrosive, and it is necessary to dry the CO$_2$ to approximately 30 parts per million of water. As a result, a dehydration step
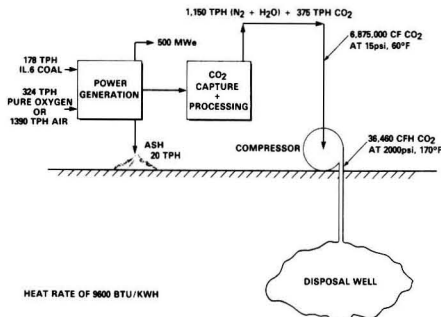
FIGURE 1. Overview of sending CO_2 from 500 MW power plant to disposal wells.

following the compression of the CO_2 is needed. One way of doing this is by scrubbing with ethylene glycol. Figure 1 shows how CO_2 compression and disposal integrates with a possible fossil energy combustion process and the relative volumes of the streams involved. The shrinkage by compression of the huge volume of CO_2 coming off of the energy conversion process is of great importance to the feasibility of the deep-well disposal technique. The 48 million standard cubic feet (SCF) of flue gas from a 500 MWt plant are reduced by separation to 6,875,000 CF of CO_2 at ambient which are then compressed for injection to 36,460 cubic feet at 2,000 psi and 170F.

Two preliminary designs and cost estimates for CO_2 compression and injection into wells for enhanced oil recovery have been reported [4, 5]. Here, the pressure of such a CO_2 stream was raised to 2,000 psi in two- or three-stage compressors with inter-stage cooling and separation of the condensed water. These cost estimates in 1986 and 1978 dollars, respectively, have been adjusted for inflation at the rate of 5% per year. After adjustment for the larger compressors that have since become available, 300 million SCFD vs. 50 million, the current estimated cost of compressing CO_2 is $8.50 per ton of CO_2 or $0.009/KWH of electricity, and the technology is available for this intermediate step.

INJECTING THE CO_2 UNDERGROUND

The injection of CO_2 into underground formations is commercially practiced for enhanced oil recovery (EOR). For application to CO_2 disposal, two capacity factors become critical; namely injection rate and holding capacity of the typical underground formation vs. the rate of discharge and the life of the typical generating plant.

The capacity of a formation to hold the emissions of a 500 MW powerplant was estimated using petroleum industry values of compressibility of rock and of salt water containing some dissolved gas and a 100-foot thick formation with 25% porosity. No account was given to the possibility of enhanced capacity due to dissolution of the CO_2 in the salt water generally found in the formation voids or as a result of possible reaction of the CO_2 with alkaline solids in the formation. Elk Hills, which meets the further elegant requirement of producing oil, is 47,000 acres. Under these circumstances, such a formation has an estimated capacity equal to the output of a 500 MW powerplant for 1.5 years, assuming no withdrawals.

The rate of injection has been estimated by Darcy law calculations for a 100-foot thick formation, permeability of 0.2 Darcy's, a down-hole dispersion pressure difference of 450 psi, and a 50,000 acre area of dispersion. These formation prop-

erties fall within the range of those reported by industry. The resultant injection rate is 1.29 million actual cubic feet of CO_2 at 180F and 2,000 psi per day vs. the 0.9 million emitted by a 500 MW generating plant. The low viscosity of the super critical CO_2 being injected is most helpful here. This method of estimation checks acceptably with field data in that estimates of injection rates predicted reasonably the rates reported for field tests of injection of CO_2 for EOR [6] and for brine injection wells operated by the U.S. Office of Strategic Oil Reserve.

Injection to depths as great as 5,000 feet would be possible since the static head of the CO_2 and compression of the CO_2 to 2,000 psi would more than offset the pressure that generally results from a hydrostatic head from the surface to the hole bottom. Bottom-hole temperatures of 140F are observed at such depths. A porous formation that is capped by a nearly impervious formation would be selected in order to be sure that leakage of the CO_2 stored in the formation did not occur. If the CO_2 source is close to the injection well, the cost of the well and piping is a small increment to the cost of the intermediate step of compressing the CO_2 stream for injection.

ELECTRIC GENERATION PROCESSES

Existing fossil-fueled generating processes are largely coal-fired boilers, and, hence, substitution of oxygen for air to facilitate separation of the CO_2 would be costly unless improved process efficiency could be introduced as a result. Higher efficiencies are attainable with IGCC, which is the focus of the work by the University of Utrecht and of our early studies. They have estimated a 30% increase in the cost of electricity for CO_2 disposal.

Other electric generation processes now in an early state of development show promise of cheaper power. A MHD-Heat Recovery (MHD-HR) process, which utilizes an oxidant enriched with oxygen, involves extraction of further power from the 3,700F exhaust gases from the MHD channel by a heat-recovery steam turbine step. In order to justify the use of an oxidant with 99% oxygen, a modified process was conceptualized utilizing two MHD channels in series in which coal was initially combusted with the quantity of 99% oxygen just sufficient to convert coal approximately to the CO stage, at which point, the inlet to the first of two MHD channels is at the desired temperature of 4,700F. Upon leaving this MHD channel, the gas was converted to the CO_2 stage by incremental oxygen which reheated it to a temperature of 4,700F for use in a second MHD channel in series. The conventional heat-recovery stage then followed. This modification not only facilitates the separation of CO_2 but also from an estimate based on first principles increases the process efficiency from about 43% to 49% which should significantly reduce the cost of electricity and facilitate CO_2 collection and disposal.

The fuel cell based electric generating plant is another concept that promises higher thermal efficiency and lower cost that also would facilitate CO_2 separation for disposal. A concept presently being investigated includes an oxygen-blown coal gasifier to supply fuel gas to the fuel cells. In the operation of fuel cells, the electrolyte layer separating the electrodes keeps the exhaust CO_2 free of the nitrogen in the reactant air. At present, designs call for mixing of this stream with diluents while recovering heat. However, system modifications can be foreseen that would keep the CO_2 separate so that it may be sent to disposal. Yet, this should not significantly affect the high estimated thermal efficiency of the process and its low cost.

Thus, there are a number of possible generating processes that offer the hope of acceptable economics after including provision for CO_2 separation and disposal. Such plants would emit only a small fraction of the CO_2 from combustion of fossil fuels.

OTHER CO₂ EMITTERS

Other large volume process industries are emitters of CO_2. These include ammonia plants and other hydrogen consumers such as potential plants for the manufacture of synthetic liquid fuels or natural gas from coal. Each of these plant configurations already emit a relatively pure CO_2 stream. As a result, the incremental cost of disposal of the CO_2 is estimated to be low—about $.60/barrel of synthetic crude, for example. This provision would largely eliminate the criticism of synthetic liquid fuels from coal that is based on higher CO_2 emission on combustion than petroleum.

UNDERGROUND CO₂ CONVERSION

Biofixation has long been recognized as a desirable way to dispose of CO_2, but an economic means of doing this is not known. However, it may be possible to combine anaerobic biofixation with the proposed underground disposal of CO_2 as an alternate method to dispose of CO_2 and possibly to produce reusable CO_2-derived fuels.

Nonphotosynthetic biofixation of CO_2 is common in nature. The porous underground formations for disposal of CO_2 could be used as the reaction vessels for this method of fixation if they contain at least trace quantities of such energy sources as coal, hydrocarbons, oil, gas, oil shale, ferrous iron, etc., that are for one reason or another uneconomic to produce. Then, such overall reactions as:

$$CH_4 + CO_2 \rightarrow (CH_2O)_{2n}$$
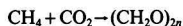
may be anticipated. Upon initiation of injection of CO_2, a suitable organism could, if necessary, be injected which would be capable of such a conversion.

While conditions in formations at the depths proposed will be somewhat severe (about 140F and 2,000 psi), numerous examples are known of similar bioactivity at such conditions [9, 10]. Such activity at temperatures as severe as 300F and comparable pressures have been observed in the case of the ocean bed hydrothermal vents and of volcanic vents under study at Mount St. Helens, WA. At the less severe conditions anticipated in this application, analogous conversions have been observed on a large scale. For example, Microbiological Enhanced Oil Recovery is being studied [11], and the occurrences of "souring" of oil wells through the reduction of sulfates to H_2S by sulfur reducing organisms injected unintentionally during water flooding has been observed. A collection including thousands of organisms isolated from comparable depths exists [12]. In one study of a bioreactor at conditions analogous to a dry underground formation, an organism supported on an inert support converted gases passed over them.

The reaction conditions which would exist upon injection of CO_2 into such formations as proposed should, in many respects, be ideal. Mixing of the CO_2 with the porous structure of the underground formation which contains the energy source would be intimate and rapid. Since the formation structure would be similar to that associated with the well-souring phenomenon noted above, it could be expected that the organism would migrate in a similar way through the formation in tandem with the CO_2 flow front. And, it is possible that the incoming super critical CO_2 will extract the oxygenates as they are produced in the formation and carry them as a concentrate to a band behind the reaction front. Then, this fuel product could be brought to the surface and concentrated further by flashing the liquid as it is produced.

LITERATURE CITED

1. Steinberg, M., et al., "A Systems Study of the Removal, Recovery and Disposal of Carbon Dioxide from Fossil Fuel Power Plants in the U.S.," U.S. DOE, DOE/CH00016-2 (1984).
2. Hendriks, C., K. Blok and W. Trurkenburg, *Climate & Energy*, Kluwer Academic Press, Dordrec, The Netherlands, pp. 125–188 (1990).
3. Radian Corporation, "Cool Water Coal Gasification Program: Final Report," Electric Power Research Institute, Palo Alto, CA; GS-6806 (1990).
4. Fluor Technology, "Coproduction of Carbon Dioxide (CO_2) and Electricity," Electric Power Research Institute, Palo Alto, CA; AP4827 (1986).
5. Pullman-Kellogg Company, "Sources and Delivery of Carbon Dioxide for Enhanced Oil Recovery," U.S. DOE FE-2515-24 (1978).
6. Pande, N. K., "A Comprehensive Study on the Use of Carbon Dioxide for Enhanced Oil Recovery," New Mexico Petroleum Recovery Research Center Report PRRC 85-41 (1985).
7. Vejtasa, S., "TAG Technical Assessment Guide, Volume 1: Electricity Supply," Electric Power Research Institute, Palo Alto, CA; P4463-SR (1986).
8. Avco Everett Res. Lab, "Parametric Study of Potential Early Commercial MHD Power Plants Task III—Parametric Variation of Plant Size," U.S. DOE, DOE/NASA/0051-3 (1981).
9. Huber, R., et al., "Hyperthermophilic Archaebacteria Within the Crater and Open-sea Plume of Erupting Macdonaid Seamount," *Nature*, 345, 179–182 (1990).
10. Klug, M. J. and C. A. Reddy, Editors; J. A. Baross, "Current Perspectives in Microbiological Ecology"; American Society for Microbiology, Washington, D.C. (1984).
11. Finnerty, W. R., et al., "Microbial Enhancement of Oil Recovery," *Biotechnology*, 1 (1), 47–54 (1983).
12. Wobber, F., "Subsurface Science Program, Program Overview and Research Abstracts," U.S. DOE, DOE/ER-0432 (1990).

Modeling, Analysis, and Simulation of Bioremediation of Soil Aggregates

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The role of aggregates and their characteristics on bioremediation in soil has received very little attention. In this investigation, the contaminated aggregates bioremediation (CAB) model has been developed and simulated to analyze the bioremediation of soil and water in the aggregates. The model equations consist of a system of three non-linear partial differential equations. Dimensional analysis of the equations has been performed. Sensitivity analysis conducted by numerically solving them has demonstrated the effects of aggregate radius, partition coefficient, and initial contaminant concentration on the time and mechanism of remediation. The rates of diffusion of substrate and oxygen, and the biodegradation-rate have been found to be the controlling mechanisms for remediation in the aggregates.

INTRODUCTION

The contamination of soil and water is one of the most pressing societal problems of recent times. Environmental models are increasingly being relied upon to facilitate evaluation and selection of the most suitable treatment scheme for their remediation [1]. They serve to bridge the gap between the theoretical understanding and practical applications. It is difficult, however, to unequivocally take into account in such models the relative roles of all the mechanisms or processes affecting the behavior of chemicals in the environment. Therefore, these models, essentially *caricatures of the real world*, include in them only the dominant factors. Nevertheless, the use of site-specific rather than generic information in constructing the models enables them to make fairly reliable predictions.

Environmental models can be classified into descriptive, physical, analogous, and mathematical models [2]. Of these, the mathematical models based on physical principles, axioms, and reasonable assumptions, i.e., the mathematical-mechanistic models, offer promising means for predicting the spatial and temporal distributions of chemicals in the natural environment [2]. These models provide a conceptual framework for objective assimilation and manipulation of the various mechanisms involved in the transport, transformation and accumulation of organic chemicals in soil; the results obtained, supplemented by the best technical judgement, would contribute to the clarification of the issues and ambiguities inherent in decision-making [3]. Nevertheless, the existing information is inadequate for large-scale field applications. The identification of dominant factors controlling the fate of pollutants in the natural environments remains elusive. An urgent need exists for a concerted effort to develop and model new soil remediation technologies.

STATE-OF-THE-ART

Ehrenfeld and Bass [4], USEPA [5], Boutwell *et al*. [3], Sims *et al*. [6], Davis and Olsen [7], Olsen and Davis [8], and Sims [9] have extensively reviewed the literature on the remediation technologies for contaminated sites. The *in situ* treatments can be effective for degradation, containment, and extraction of pollutants. They are applicable, mainly, to the unsaturated zone, but can be applied to the saturated zone with some modifications. Numerous transport models have been proposed to represent the migration of contaminants through the porous media [10, 11, 12, 13, 14, 15, 16, 17]. EPRI [18] has provided an excellent review of multiphase flow models.

Sorption, convective-dispersive flux, and chemical-biological transformations are three important processes controlling the ultimate fate and transport of chemicals in the environment [19]. Reviews by Weber and Smith [20], Brusseau and Rao [21], and Harmon et al. [22] have discussed the implications of sorption mechanisms on organic transport modeling. The mass transfer resistances either due to the physical barrier or due to some chemical reactions in contaminated-porous systems can be meaningfully described by resorting to nonequilibrium models. The equilibrium and nonequilibrium models have been compared for transport of solute affected by surface reactions [23]. Jennings and Kirkner [24] and Valocchi [25] have confirmed the validity of the local equilibrium assumption in the transport models under varying flow dynamics. A model has been developed by Cameron and Klute [26] to depict the adsorption of a chemical by a combination of equilibrium and nonequilibrium kinetic models.

The majority of available transport models take into account the convection-dispersion flux by resorting to the classical convection-dispersion equations [27]. A diagnostic model has been developed for efficiently utilizing the experimental data directly in numerical simulations [28]. Grisak and Pickens [29] have described the effect of matrix diffusion on the transport of solute through porous media. These and many other models consider the system to be homogeneous and isotropic [30, 31]. The bimodal flow of contaminants has been explained by partitioning the porous media into two compartments, namely, mobile and immobile [32, 33]. Little attention has been focussed on the effect of aggregate characteristics in the bed.

The void in a porous medium typically consists of a mobile phase in the relatively large pores, i.e., the macrovoids, and an immobile phase entrapped in the relatively small pores, i.e., the microvoids. Dispersion and convection dominate the transport in the macrovoids, whereas diffusion accounts for the transport in the immobile phase. Rao et al. [34, 35], Crittenden et al. [36], Goltz and Roberts [37, 38], Roberts et al. [39], and Fong and Mulkey [40] have simulated the transport of solute through the aggregated medium. Pellet [41], Satterfield et al. [42], Prasher and Ma [43], and Ball and Roberts [44] have investigated the importance of diffusivity of solute and its adsorption in the aggregates for describing the dynamics of fixed beds. According to Mackay and Cherry [45], numerous aquifers contain thin beds of silt and clay in which transport by diffusion is appreciable. They have indicated that when the contaminants have been present for a long period of time, they are carried into the clayey strata by diffusion. Because of the relatively high porosity and low permeability of clayey strata, diffusion must be considered in modeling the bioremediation of contaminants in these soil aggregates.

A meaningful portrayal of flow physics of contaminants for predicting their attenuation during migration in the subsurface zone should include a proper characterization of the degradation. The contaminants present inside the aggregates can be attenuated either by chemical and/or biological reactions. Grenny et al. [30], Wu et al. [46], and Janssen et al. [47] have modeled the nonbiological transformations in the porous media. Biodegradation of organics has been modeled by a number of researchers [48, 49, 50, 51, 52, 53, 54, 31]. Extensive bibliographies can be found in the treatise edited by Scholze et al. [55] on biotechnology for degradation of toxic chemicals in hazardous waste and also in Sims et al. [56]. A comparison has been made between the instantaneous reaction model and a kinetic reaction model for biodegradation in investigating the significance of oxygen utilization rate in biodegradation [57]. Kindred and Celia [58] have developed a model to account for both aerobic and anaerobic decay of contaminants.

A number of mathematical models have been proposed for describing the growth and transport of microorganisms in the porous media. Baveye and Valocchi [59] have described and evaluated the three main frameworks to model the morphology of microorganisms in porous media. These frameworks are discrete microcolonies attached to the particle surfaces, continuous biofilms on the particle surface, and simple partitioning between the attached microorganisms on the surface and pore liquid with the absence of any pore scale geometrical configurations of attached microorganisms. Characklis and Marshall [60] and Cunningham et al. [61] have considered the importance of the role of microbial films in porous media in in situ bioremediation. When the contaminant concentration is low, the film thickness is limited by the availability of substrate for growth and biomass accumulation.

Although numerous models are available in the literature, none attempts to describe the combined effects of diffusion, adsorption, and biodegradation inside the aggregates. Rasmuson [62] has developed a model to elucidate first-order degradation in aggregates with a variable size and shape. In the present study, for the first time, a model has been developed and simulated to describe the biological transformations, adsorption, and diffusion of organic chemicals inside the aggregates and identify some of the principal factors controlling the time and mechanism of remediation in the aggregates.

CAB MODEL

Microorganisms are ubiquitous and are present at appreciable depths in the subsurface zone [63, 64]. They utilize organic contaminants as a carbon and energy source. The CAB model takes into account the ability of naturally occurring microorganisms to attenuate the contaminants in the subsurface. The influence of aggregate radius, initial substrate concentration, and partition coefficient of the substrate on the fate of chemicals has been investigated. Results obtained from this investigation will identify the governing mechanisms under different test cases. The time scales for remediation of aggregates under ideal conditions will be obtained from numerical simulations.

Assumptions

The CAB model considers that organic contaminants are uniformly deposited in soil aggregates. Moreover, it considers that the microorganisms are present as suspended forms in the pore liquid and are also attached as microcolonies to the solid surface; they grow by consuming organic contaminants and oxygen.

The following major assumptions are imposed while deriving the model: (a) The bed is composed of spherical soil aggregates of a single size; (b) the aggregates are saturated, homogeneous and isotropic and are made up of solid particles and aqueous solution; (c) the temperature is constant in the bed; (d) the reaction rate follows the Monod kinetic model (Bailey and Ollis [65]) and depends only on the concentrations of three components, oxygen, biomass, and substrate; (e) transport in the aggregate is by diffusion only; (f) the transport resistances of substrate and oxygen to and through the microcolonies attached to the surface of soil particles are negligible; therefore, the microcolonies respond to the variations in the bulk concentrations in the pore liquid; and (g) the flow rate of oxygen-rich water having a zero concentration of substrate and a low value of biomass is sufficiently high in the macrovoids of the bed; this maintains fixed concentrations of substrate, oxygen, and biomass at the exterior of the aggregate at $r = R$.

Derivation

The mass balance of component i in a spherical aggregate gives rise to

$$\epsilon_a \frac{\partial C_{i,pt}}{\partial t} + \rho \frac{\partial q_i}{\partial t} = \frac{D_{i,pt}\epsilon_a}{\tau r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_{i,pt}}{\partial r}\right)$$

$$+\frac{D_{i,so}}{r^2}\rho\frac{\partial}{\partial r}\left(r^2\frac{\partial q_i}{\partial r}\right)+\epsilon_a r_i^{pt}+\rho r_i^{sf} \quad (1)$$

where subscript i stands for substrate, oxygen, and biomass. The dissolved concentration, $C_{i,pt}$, and the adsorbed concentration, q_i, are related through the local adsorption-desorption equilibrium in the aggregate which can be expressed as

$$q_i=K_{di}C_{i,pt} \quad (2)$$

Substituting this equation into Eq. 1 leads to

$$(\epsilon_a+\rho K_{di})\frac{\partial C_{i,pt}}{\partial t}=\frac{D_{i,pt}\epsilon_a/\tau+D_{i,so}\rho K_{di}}{r^2}$$
$$\times\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{i,pt}}{\partial r}\right)+\epsilon_a r_i^{pt}+\rho r_i^{sf} \quad (3)$$

This is the general equation for component i in the aggregate. The reaction terms for substrate, oxygen and biomass are expressed in terms of the Monod model. The rate of substrate consumption by the microorganisms in the pore liquid, $-r_s^{pt}$, is expressed as

$$-r_s^{pt}=\frac{\mu_m}{Y_s}C_{b,pt}\left(\frac{C_{s,pt}}{K_s+C_{s,pt}}\right)\left(\frac{C_{o,pt}}{K_o+C_{o,pt}}\right) \quad (4)$$

where subscripts s, o, and b refer to the substrate, oxygen, and biomass, respectively. The rate of substrate consumption by the microcolonies attached to the surface of soil particles, $-r_s^{sf}$, is

$$-r_s^{sf}=\frac{\mu_m}{Y_s}q_b\left(\frac{C_{s,pt}}{K_s+C_{s,pt}}\right)\left(\frac{C_{o,pt}}{K_o+C_{o,pt}}\right) \quad (5)$$

The rate of oxygen consumption in the pore liquid space, $-r_o^{pt}$, and that on the surface of soil particles, $-r_o^{sf}$, are expressed, respectively, as

$$-r_o^{pt}=\frac{\mu_m}{Y_o}C_{b,pt}\left(\frac{C_{s,pt}}{K_s+C_{s,pt}}\right)\left(\frac{C_{o,pt}}{K_o+C_{o,pt}}\right) \quad (6)$$

$$-r_o^{sf}=\frac{\mu_m}{Y_o}q_b\left(\frac{C_{s,pt}}{K_s+C_{s,pt}}\right)\left(\frac{C_{o,pt}}{K_o+C_{o,pt}}\right) \quad (7)$$

The rate of biomass growth in the form of suspended microorganisms in the pore liquid, r_b^{pt}, and that at the interface, r_b^{sf}, are expressed, respectively, as

$$r_b^{pt}=\mu_m C_{b,pt}\left(\frac{C_{s,pt}}{K_s+C_{s,pt}}\right)\left(\frac{C_{o,pt}}{K_o+C_{o,pt}}\right)-k_d C_{b,pt} \quad (8)$$

$$r_b^{sf}=\mu_m q_b\left(\frac{C_{s,pt}}{K_s+C_{s,pt}}\right)\left(\frac{C_{o,pt}}{K_o+C_{o,pt}}\right)-k_d q_b \quad (9)$$

Substituting the above kinetic expressions for substrate consumption, Eqs. 4 and 5, and the equilibrium relation, Eq. 2, into Eq. 3 gives rise to

$$(\epsilon_a+\rho K_{ds})\frac{\partial C_{s,pt}}{\partial t}=\frac{D_{s,pt}\epsilon_a/\tau+D_{s,so}\rho K_{ds}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{s,pt}}{\partial r}\right)$$
$$-(\epsilon_a+\rho K_{db})\frac{\mu_m}{Y_s}C_{b,pt}\left(\frac{C_{s,pt}}{K_s+C_{s,pt}}\right)\left(\frac{C_{o,pt}}{K_o+C_{o,pt}}\right) \quad (10)$$

The adsorption of oxygen in the solid phase is neglected; thus,

$$\epsilon_a\frac{\partial C_{o,pt}}{\partial t}=\frac{D_{o,pt}\epsilon_a}{\tau r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{o,pt}}{\partial r}\right)$$
$$-(\epsilon_a+\rho K_{db})\frac{\mu_m}{Y_o}C_{b,pt}\left(\frac{C_{s,pt}}{K_s+C_{s,pt}}\right)\left(\frac{C_{o,pt}}{K_o+C_{o,pt}}\right) \quad (11)$$

The diffusion of biomass on the solid phase is negligible; hence, $D_{b,so}=0$ and

$$(\epsilon_a+\rho K_{db})\frac{\partial C_{b,pt}}{\partial t}=\frac{D_{b,pt}\epsilon_a}{\tau r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{b,pt}}{\partial r}\right)$$
$$+(\epsilon_a+\rho K_{db})\mu_m C_{b,pt}\left(\frac{C_{s,pt}}{K_s+C_{s,pt}}\right)\left(\frac{C_{o,pt}}{K_o+C_{o,pt}}\right)$$
$$-(\epsilon_a+\rho K_{db})k_d C_{b,pt} \quad (12)$$

Equations 10 through 12 are the governing equations for the CAB model. The effects of model parameters can be clarified further by transforming these equations into dimensionless forms. Thus, the following dimensionless variables and parameters are defined.

$$\overline{C}_{b,pt}=\frac{C_{b,pt}R_b}{C_{s,pt}^o R_s Y_s},\quad \overline{C}_{o,pt}=\frac{C_{o,pt}}{C_{o,pt}^f},\quad \overline{C}_{s,pt}=\frac{C_{s,pt}}{C_{s,pt}^o},\quad \overline{r}=\frac{r}{R},$$

$$\theta=\frac{t}{\theta_r},\quad \phi_1=\frac{R}{3}\sqrt{\frac{\mu_m\tau C_{s,pt}^o C_{o,pt}^f}{K_s K_o D_{s,pt}}},\quad \phi_2=\frac{R}{3}\sqrt{\frac{k_d\tau}{D_{s,pt}}},$$

$$\beta_o=\frac{C_{o,pt}^f}{K_o},\quad \beta_s=\frac{C_{s,pt}^o}{K_s},\quad R_b=1+\frac{\rho K_{db}}{\epsilon_a}$$

$$R_s=1+\frac{\rho K_{ds}}{\epsilon_a},\quad \theta_r=\frac{R^2\tau}{D_{s,pt}},\quad W=\frac{C_{s,pt}^o R_s Y_s}{C_{o,pt}^f Y_o},$$

$$\overline{D}_s=\frac{D_{s,pt}/\tau+D_{s,so}(R_s-1)}{D_{s,pt}/\tau},\quad \overline{D}_o=\frac{D_{o,pt}}{D_{s,pt}},\quad \overline{D}_b=\frac{D_{b,pt}}{D_{s,pt}}$$

In these dimensionless expressions, $C_{s,pt}^o$ is the initial concentration of substrate in the bed, and $C_{o,pt}^f$ is the concentration of oxygen at the exterior of the aggregate. Substitution of the dimensionless variables in Eqs. 10, 11, and 12 yields, respectively,

$$\frac{\partial\overline{C}_{s,pt}}{\partial\theta}=\frac{\overline{D}_s}{R_s}\left(\frac{2}{\overline{r}}\frac{\partial\overline{C}_{s,pt}}{\partial\overline{r}}+\frac{\partial^2\overline{C}_{s,pt}}{\partial\overline{r}^2}\right)$$
$$-9\phi_1^2\overline{C}_{b,pt}\left(\frac{\overline{C}_{s,pt}}{1+\beta_s\overline{C}_{s,pt}}\right)\left(\frac{\overline{C}_{o,pt}}{1+\beta_o\overline{C}_{o,pt}}\right) \quad (13)$$

$$\frac{\partial\overline{C}_{o,pt}}{\partial\theta}=\overline{D}_o\left(\frac{2}{\overline{r}}\frac{\partial\overline{C}_{o,pt}}{\partial\overline{r}}+\frac{\partial^2\overline{C}_{o,pt}}{\partial\overline{r}^2}\right)$$
$$-9\phi_1^2 W\overline{C}_{b,pt}\left(\frac{\overline{C}_{s,pt}}{1+\beta_s\overline{C}_{s,pt}}\right)\left(\frac{\overline{C}_{o,pt}}{1+\beta_o\overline{C}_{o,pt}}\right) \quad (14)$$

$$\frac{\partial\overline{C}_{b,pt}}{\partial\theta}=\frac{\overline{D}_b}{R_b}\left(\frac{2}{\overline{r}}\frac{\partial\overline{C}_{b,pt}}{\partial\overline{r}}+\frac{\partial^2\overline{C}_{b,pt}}{\partial\overline{r}^2}\right)$$
$$+9\phi_1^2\overline{C}_{b,pt}\left(\frac{\overline{C}_{s,pt}}{1+\beta_s\overline{C}_{s,pt}}\right)\left(\frac{\overline{C}_{o,pt}}{1+\beta_o\overline{C}_{o,pt}}\right)-9\phi_2^2\overline{C}_{b,pt} \quad (15)$$

The dimensionless numbers, ϕ_1 and ϕ_2, are the *Thiele moduli* for the growth and decay of biomass, respectively; β_o and β_s, the *saturation parameters* for oxygen and substrate, respectively; R_b and R_s, the *retardation factors* for biomass and substrate, respectively; and W, the *oxygen supply factor* [31].

FIGURE 1. Concentrations in the aggregate vs. time for case 1 at $\bar{r} = 0$; $R_s = 8$, $W = 200$, $\phi_1 = 588$, $\beta_s = 400$:

—————————— Biomass
- - - - - - - - - Oxygen
——— - ——— Substrate

FIGURE 3. Concentrations in the aggregate vs. time for case 3 at $\bar{r} = 0$; $R_s = 698$, $W = 175$, $\phi_1 = 59$, $\beta_s = 4$:

—————————— Biomass
- - - - - - - - - Oxygen
——— - ——— Substrate

Simulation

The coupled set of partial differential equations, Eqs. 13, 14, and 15, have been integrated by the IMSL subroutine DPDES [66]. The algorithm is based on the method of lines and employs a series of cubic hermite polynomials to obtain the solution. The number of mesh points and the time step size affect the accuracy of the solution. Simulations have been conducted with different numbers of mesh points and with different time step sizes to check the accuracy of the simulation. In performing the simulations, emphasis has been on sensitivity analysis to study the mechanisms involved, and the effect of retardation factor, oxygen supply factor, and the Thiele moduli on the total time of remediation, T_b.

RESULTS AND DISCUSSION

During each run, the simulation was terminated as soon as the contaminant concentration throughout the aggregate

FIGURE 2. Concentration profiles in the aggregate for case 1 at $\theta = 1$; $R_s = 8$, $W = 200$, $\phi_1 = 588$, $\beta_s = 400$:

—————————— Biomass
- - - - - - - - - Oxygen
——— - ——— Substrate
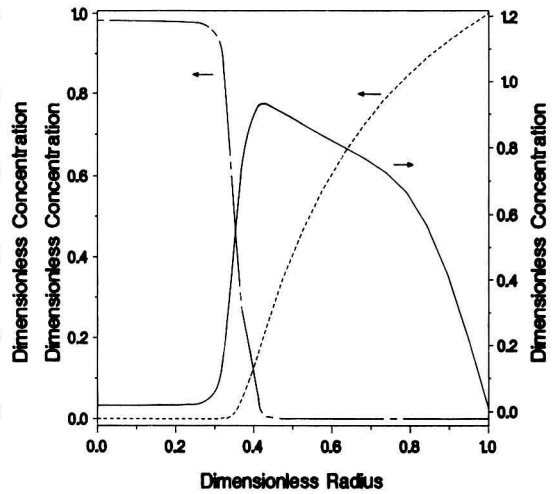
FIGURE 4. Concentration profiles in the aggregate for case 3 at $\theta = 4$; $R_s = 698$, $W = 175$, $\phi_1 = 59$, $\beta_s = 4$:

—————————— Biomass
- - - - - - - - - Oxygen
——— - ——— Substrate
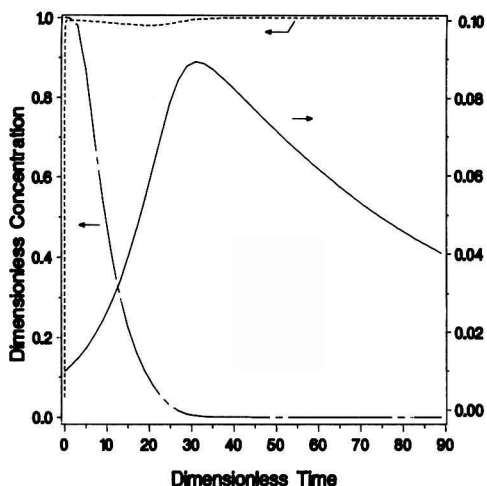
FIGURE 5. Concentrations in the aggregate vs. time for case 5 at $\bar{r} = 0$; $R_s = 71$, $W = 177$, $\phi_1 = 18.6$, $\beta_s = 40$:

——————— Biomass
- - - - - - - - - Oxygen
——— - ——— Substrate

reached 1 $\mu g/kg$ or below, and T_b was determined. The appropriate initial and boundary conditions for this numerical simulation were as follows:

At $\theta = 0$, $\quad \bar{C}_{o,pt} = 0.05$, $\quad \bar{C}_{s,pt} = 1.00$, $\quad \bar{C}_{b,pt} = \bar{C}_b^o$,

$$\text{for } 0 \leq \bar{r} \leq 1$$

At $\bar{r} = 0$, $\quad \dfrac{\partial \bar{C}_{i,pt}}{\partial \bar{r}} = 0$, $\quad i = o, s, b$, $\quad \text{for } \theta \geq 0$

At $\bar{r} = 1$, $\quad \bar{C}_{o,pt} = 1.00$, $\quad \bar{C}_{s,pt} = 0$, $\quad \bar{C}_{b,pt} = \bar{C}_b^o$, $\quad \text{for } \theta > 0$
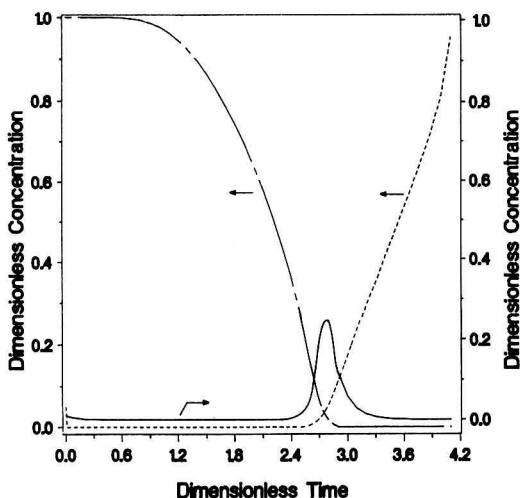
FIGURE 6. Concentrations in the aggregate vs. time for case 6 at $\bar{r} = 0.5$; $R_s = 71$, $W = 177$, $\phi_1 = 1860$, $\beta_s = 40$:

——————— Biomass
- - - - - - - - - Oxygen
——— - ——— Substrate

FIGURE 7. Concentration profiles in the aggregate for case 6 at $\theta = 3.8$; $R_s = 71$, $W = 177$, $\phi_1 = 1860$, $\beta_s = 40$:

——————— Biomass
- - - - - - - - - Oxygen
——— - ——— Substrate

The results of simulation are presented in Figures 1 through 11. The bioremediation times for the concentration of the adsorbed substrate to drop below 1 ppb at the center of the aggregate for the 10 cases investigated are listed in Tables 1 and 2. The times taken by the contaminants to diffuse out of the aggregate, T_d, are also given in these tables. The values of T_d have been determined by solving Eq. 13 for the limiting cases without bioremediation. The results of simulation indicate that diffusion of oxygen into the aggregate and the retardation of contaminant transport in the aggregate affect significantly the time of remediation in the aggregates. Figures 1, 3, and 10 show that in the early stages of the simulation, oxygen diffuses into the aggregate faster than it is consumed. As the biomass concentration increases, oxygen is consumed faster than it is supplied, and the oxygen concentration decreases to a value close to zero.

Figures 1 through 4 reveal the effect of retardation factor, R_s, on the fate of chemicals. When the partition coefficient, or equivalently, the retardation factor, is small, the diffusion of substrate out of the aggregate is very rapid (Figures 1 and 2). Note that the degradation of contaminants takes place mainly near the exterior of the aggregate. A large retardation factor makes less substrate available in the liquid phase, thereby reducing the consumption rate of contaminants. An increase in the retardation factor decelerates the diffusion of substrate in the aggregate; the oxygen front moving through the aggregate by diffusion is the controlling mechanism for remediation (Figures 3 and 4). The maximum biomass growth takes place at the point where both oxygen and substrate are available (Figure 4). The diffusion time is much greater than the bioremediation time when the value of retardation factor is large (Table 1).

Figures 5 through 7 reveal the effect of aggregate radius on the rate controlling mechanism of bioremediation. For a small aggregate radius, or equivalently, a small Thiele modulus, the oxygen diffuses rapidly inside the aggregate (Figure 5). The attenuation of chemicals in the *spherical microbiological incinerator* is essentially uniform because it is controlled by the rate of degradation. As the Thiele modulus increases, the diffusion of oxygen into the aggregate becomes rate limiting. The
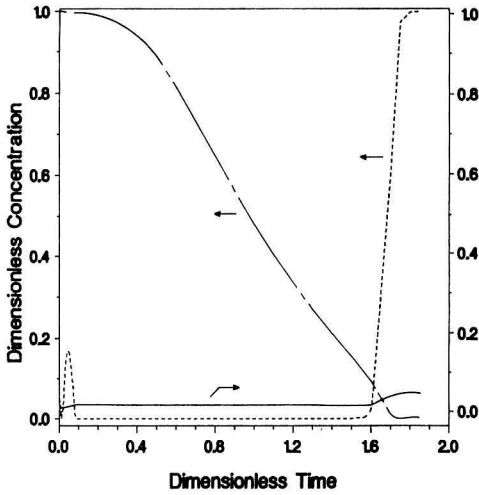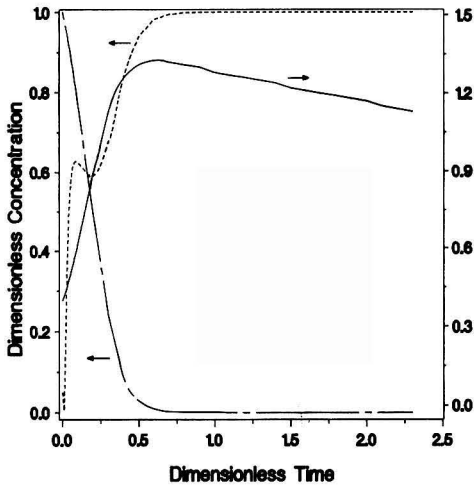
FIGURE 8. Concentrations in the aggregate vs. time for case 7 at $\bar{T} = 0$; $R_s = 71$, $W = 4.4$, $\phi_1 = 29$, $\beta_s = 1$:

——————————— Biomass
– – – – – – – – – Oxygen
———— – ———— Substrate
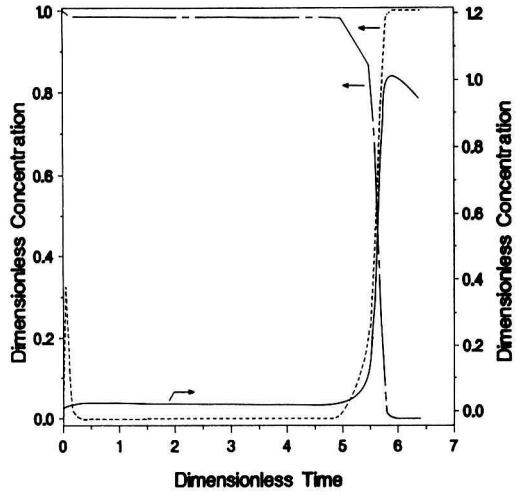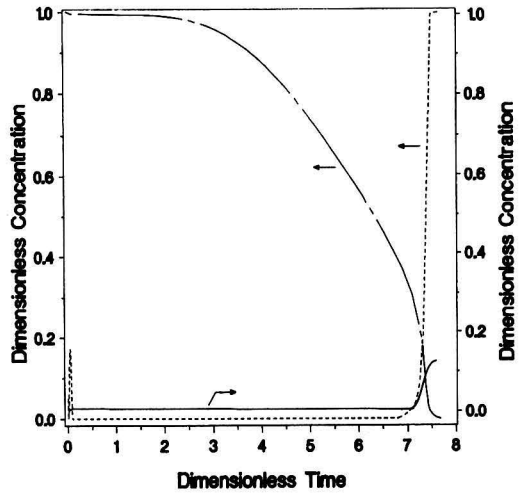

FIGURE 10. Concentrations in the aggregate vs. time for case 9 at $\bar{T} = 0$; $R_s = 71$, $W = 444$, $\phi_1 = 294$, $\beta_s = 100$:

——————————— Biomass
– – – – – – – – – Oxygen
———— – ———— Substrate

oxygen moves extremely slowly in large aggregates, thereby prolonging substantially the time for remediation. The biomass production rate is small due to the low availability of oxygen and substrate together for consumption. Endogenous metabolism is observed distinctly, which further reduces the biomass concentration (Figures 6 and 7). An increase in the Thiele modulus transforms the overall remediation process from being reaction controlled to diffusion controlled.

A small initial contaminant concentration requires a small oxygen supply factor, thus rendering the overall process to be reaction limited (Figures 8 and 9). The oxygen requirement being low, the oxygen is made available rapidly in the aggregate, and the reaction in the aggregate proceeds quite uniformly. A larger initial contaminant concentration requires more oxygen. Figures 10 and 11 demonstrate that for a large initial contaminant concentration, the rate of contaminant diffusion out of the aggregate is significant; microbial growth occurs in the region where both oxygen and substrate are present. As the contaminant concentration decreases, the zone of active growth moves further towards the center of the aggregate
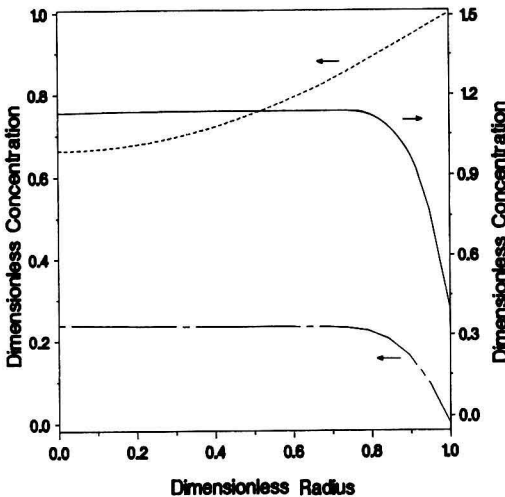
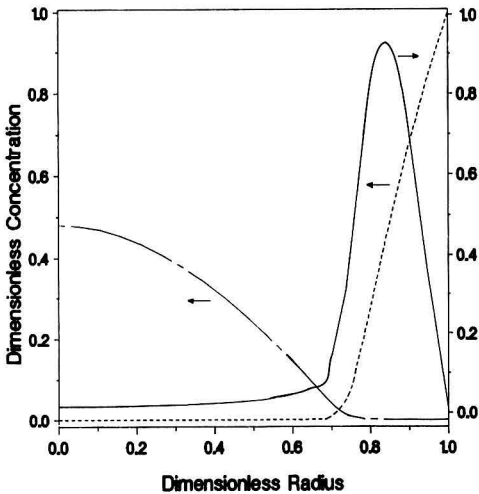

FIGURE 9. Concentration profiles in the aggregate for case 7 at $\theta = 0.3$; $R_s = 71$, $W = 4.4$, $\phi_1 = 29$, $\beta_s = 1$:

——————————— Biomass
– – – – – – – – – Oxygen
———— – ———— Substrate
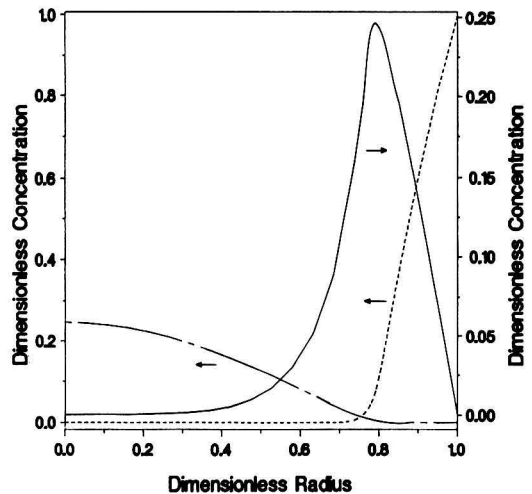
FIGURE 11. Concentration profiles in the aggregate for case 10 at $\theta = 13.5$; $R_s = 71$, $W = 4437$, $\phi_1 = 930$, $\beta_s = 1000$:

——————————— Biomass
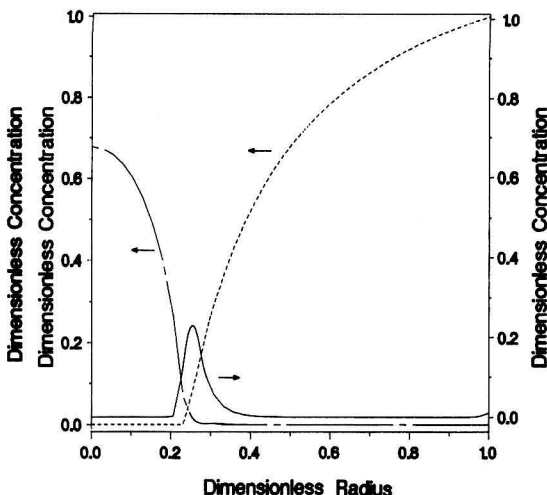– – – – – – – – – Oxygen
———— – ———— Substrate

Table 1 Effect of Partition Coefficient and Aggregate Radius on the Time Required for Remediation in the Aggregate

Case No.	Initial Substrate Concentration q_s^o, mg/kg	Radius of Aggregate R, cm	Partition Coefficient K_{ds}, cm³/g	Bioremediation Time T_b, days	Diffusion Time T_d, days
1	600	1	1.5	7.3	46.0
2	600	1	15	17.4	407.1
3	600	1	150	24.7	4012.8
4	600	1	1500	41.3	40073.8
5	600	0.1	15	2.2	4.1
6	600	10	15	1660.9	40641.7

Table 2 Effect of Initial Substrate Concentration on the Time Required for Remediation in the Aggregate

Case No.	Initial Substrate Concentration q_s^o, mg/kg	Radius of Aggregate R, cm	Partition Coefficient K_{ds}, cm³/g	Bioremediation Time T_b, days	Diffusion Time T_d, days
7	15	1	15	4.0	287.6
8	150	1	15	6.5	354.4
2	600	1	15	17.4	407.1
9	1500	1	15	31.2	421.3
10	15000	1	15	83.9	488.1

(Figure 11). Because of endogenous metabolism, the dimensionless concentration of biomass is relatively small in Figures 10 and 11. Biomass accumulation does not appear to be sufficient to affect the diffusivity of oxygen. For a large initial substrate concentration, the saturation parameter, β_s, is also large, thus indicating that the reaction is zero order with respect to substrate, and is controlled by the rate of oxygen diffusion into the aggregate.

All simulations have been carried out until the adsorbed concentration of substrate at the center of the aggregate becomes smaller than 1 ppb. The buildup of biomass is low when the initial concentration of contaminant is low. This reduces the biodegradation rate, thereby prolonging the time of remediation. The bioremediation times in the aggregate obtained by varying the partition coefficient, radius of aggregate, and initial substrate concentration are listed in Tables 1 and 2. The values of the remaining parameters for simulation are summarized in Table 3. To render the numerical values of the parameters as realistic as possible, literature values were extensively reviewed. While a multitude of sources are available for several of the parameters, only one of the sources is listed for each of these parameters on the basis that the values obtained are realistic within the range of experimental conditions.

In Tables 1 and 2, the bioremediation time is less than the time required for the contaminants to diffuse out of the aggregates, T_d, for all of the cases. When the partition coefficient is large, the diffusion time is much larger than the bioremediation time. The results of simulation in Tables 1 and 2 indicate that treatment methods which transport oxygen and nutrients to the surface of aggregates are superior to pump and treat methods which depend upon the surface treatment of effluent pumped from the contaminated region. Thus, when strata of silt and clay are present, stimulating bioremediation within the strata has the potential to reduce the treatment time compared to diffusion of the contaminant out of the strata. When highly contaminated aggregates, each with a radius of 1 cm or larger are present, any process capable of reducing the sizes of these aggregates will decrease the bioremediation time significantly.

Table 3 Parameter Values for Numerical Simulation*

Parameter	Value	Reference
$C_{b,pl}^o$	1.0×10^{-7} g/cm³	Dhawan *et al.* [67]
$C_{o,pl}^f$	8.0×10^{-6} g/cm³	Bailey and Ollis [65]
$D_{b,pl}$	1.0×10^{-6} cm²/s	Lauffenburger and Calcagno [68]
$D_{o,pl}$	2.0×10^{-5} cm²/s	Bailey and Ollis [65]
$D_{s,pl}$	4.0×10^{-6} cm²/s	Perry and Green [69]
$D_{s,so}$	0	
k_d	2.78×10^{-7}/s	Bailey and Ollis [65]
K_o	1.0×10^{-8} g/cm³	Johnson [70]
K_s	1.0×10^{-6} g/cm³	Bailey and Ollis [65]
K_{db}	30.0 cm³/g	Gray and Parkinson [71]
Y_o	1.0 g/g	Bailey and Ollis [65]
Y_s	0.5 g/g	Bailey and Ollis [65]
ϵ_a	0.37	Hausenbuiller [72]
μ_m	2.78×10^{-5}/s	Bailey and Ollis [65]
ρ	1.72 g/cm³	Hausenbuiller [72]
τ	1.4	Bailey and Ollis [65]

*The diffusion coefficient for biomass includes a contribution for cell motility. Surface diffusion of contaminant was neglected in the numerical simulation.

CONCLUSIONS

The bioremediation of soil aggregates has been simulated based on the newly developed CAB model. The results of simulation indicate that microbiological degradation of contaminants within the aggregate may play a significant role in remediation; most of the contaminants which are present initially within the aggregates are consumed before they reach the outer surface; and there exists a region of active biodegradation where the oxygen diffusing in and contaminant diffusing out provide sufficiently large concentrations to support microbial growth. This region where active microbial consumption occurs moves inwards with time until it reaches the center of each aggregate. For strongly adsorbed contaminants, the time required for all of the organic compound to diffuse from the aggregate far exceeds the bioremediation time. By resorting to the results obtained from the CAB model, preliminary evaluations and screening of treatment schemes may be performed using site characterization data on the contaminant concentration, contaminant adsorption, and thickness of any beds of silt or clay. The CAB model can be simulated to estimate the remediation time if reasonable values of the diffusivities and the kinetic parameters for biodegradation are available.

ACKNOWLEDGEMENT

NOTATION

$\overline{C}^o_{b,p\ell}$ = dimensionless concentration of biomass originally present in the pore liquid

$C_{i,p\ell}$ = concentration of component i in the pore liquid, M/L^3

$\overline{C}_{i,p\ell}$ = dimensionless concentration of component i in the pore liquid

$C^f_{o,p\ell}$ = concentration of oxygen at the exterior of the aggregate, M/L^3

$\overline{D}_i$ = dimensionless diffusion coefficient of component i

$D_{i,p\ell}$ = diffusion coefficient of component i in the pore liquid, L^2/T

$D_{i,so}$ = surface diffusion coefficient of component i in the solid phase, L^2/T

k_d = reaction rate constant for the decay of biomass, T^{-1}

K_o = saturation constant of oxygen, M/L^3

K_s = saturation constant of substrate, M/L^3

K_{di} = linear partition coefficient for component i, L^3/M

q_i = concentration of component i in the solid phase, M/M

r = radial position in the aggregate, L

R = radius of the aggregate, L

R_i = retardation factor for component i

$R^{p\ell}_i$ = reaction rate in the liquid phase, $M/L^3/T$

r^{sf}_i = reaction rate at the interface, $M/M/T$

t = time, T

T_d = time taken to diffuse the substrate out of the aggregate, T

T_b = time of bioremediation of the aggregate, T

W = oxygen supply factor

Y_o = yield factor of oxygen, M/M

Y_s = yield factor of substrate, M/M

Greek Letters

β_i = saturation parameter of component i

ϵ_a = volumetric fraction of liquid in the aggregate

μ_m = maximum specific growth rate of biomass, T^{-1}

ρ = bulk density of the aggregate particle, M/L^3

θ = dimensionless time

θ_r = characteristic time for diffusion, T

ϕ_1 = Thiele modulus for the growth of biomass

ϕ_2 = Thiele modulus for the decay of biomass

τ = tortuosity of pores in the aggregate

Superscripts and Subscripts

i = b, o, s for biomass, oxygen, and substrate, respectively

$p\ell$ = pore liquid

sf = interface

so = solid phase

LITERATURE CITED

1. Wood, W. P., "Role of Environmental Transport and Fate Models in Implementing the Toxic Substances Control Act," in *Modeling the Fate of Chemicals in the Aquatic Environment*, K. L. Dickson, A. W. Maki, and J. Cairns, Jr., eds., pp. 49–58, Ann Arbor Science, Michigan, 1982.
2. Yeh, G. T., "Modeling the Distribution of Chemicals in Aquatic Environments," in *Modelling the Fate of Chemicals in the Aquatic Environment*, K. L. Dickson, A. W. Maki, and J. Cairns, Jr., eds., pp. 35–48, Ann Arbor Science, Ann Arbor, Michigan, 1982.
3. Boutwell, S. H., S. M. Brown, B. R. Roberts, and D. F. Atwood, Modeling Remedial Actions at Uncontrolled Hazardous Waste Sites, pp. 1–17, Noyes Publications, New Jersey, 1986.
4. Ehrenfeld, J. and J. Bass, Handbook for Evaluating Remedial Action Technology Plans, EPA-600/2-83-076, Municipal Environmental Research Laboratory, Cincinnati, Ohio, and Office of Research and Development, Cincinnati, Ohio, 1983.
5. USEPA, Handbook Remedial Actions at Waste Disposal Sites (Revised), EPA/625/6-85/006, Office of Research and Development, Hazardous Waste Engineering Laboratory, Cincinnati, Ohio, and Office of Emergency and Remedial Response, Washington, D.C., 1985.
6. Sims, R., D. Sorensen, J. Sims, J. McLean, R. Mahmood, R. Dupont, J. Jurinak, and K. Wagner, Contaminated Surface Soils In-place Treatment Techniques, Noyes, Publications, New Jersey, 1986.
7. Davis, A. and R. L. Olsen, "Predicting the Fate and Transport of Organic Compounds in Groundwater Part 2," Hazardous Materials Control, 3(4), 18–37 (1990).
8. Olsen, R. L. and A. Davis, "Predicting the Fate and Transport of Organic Compounds in Groundwater Part 1," Hazardous Materials Control, 3(3), 38–64 (1990).
9. Sims, R. C., "Soil Remediation Techniques at Uncontrolled Hazardous Waste Sites A Critical Review," J. of the Air & Waste Management Association, 40, 704–732.
10. Crittenden, J. C., B. W. C. Wong, W. E. Thacker, V. L. Snoeyink, and R. L. Hinrichs, "Mathematical Model of Sequential Loading in Fixed-bed Absorbers," J. Water Pollution Control Fed., 52, 2780–2795 (1980).

11. Parker, J. C. and M. Th. van Genuchten, "Flux-Averaged and Volume-Averaged Concentrations in Continuum Approaches to Solute Transport," Water Resources Research, 20, 866-872 (1984).
12. Myers, T. E. and R. M. Bricka, "Modeling Ammonia Gas Transport From Solidified Hazardous Waste," Environmental Progress, 4, 187-198 (1985).
13. Freeman, R. A. and J. M. Schroy, "Modeling the Transport of 2, 3, 7, 8-TCDD and Other Volatility Chemicals in Soils," Environmental Progress, 5, 28-33 (1986).
14. Pinder, G. F. and L. M. Abriola, "On the Simulation on Nonaqueous Phase Organic Compounds in the Subsurface," Water Resources Research, 22, 109S-119S (1986).
15. Hills, R. G., I. Porro, D. B. Hudson, and P. J. Wierenga, "Modeling One-Dimensional Infiltration Into Very Dry Soils 1. Model Development and Evaluation," Water Resources Research, 25, 1259-1269 (1989).
16. Sleep, B. E. and J. F. Sykes, "Modeling the Transport of Volatile Organics in Variably Saturated Media," Water Resources Research, 25, 81-92 (1989).
17. Thorstenson, D. C. and D. W. Pollock, "Gas Transport in Unsaturated Zones: Multicomponent Systems and the Adequacy of Fick's Laws," Water Resources Research, 25, 477-507 (1989).
18. EPRI, Multiphase Flow and Transport Models for Organic Chemicals: A Review and Assessment, prepared by The University of Michigan, Dept. of Civil Eng., Ann Arbor, Michigan, EA-5976, Electric Power Research Institute, Palo Alto, California, 1988.
19. Lee, M. D., Biodegradation of Organic Contaminants in the Subsurface of Hazardous Waste Sites, Ph.D. Dissertation, Rice University, 1986.
20. Weber, W. J., Jr., and E. H. Smith, "Simulation and Design Models for Adsorption Processes," Environ. Sci. Technol., 21, 1040-1050 (1987).
21. Brusseau, M. L., and P. S. C. Rao, "Sorption Nonideality during Organic Contaminant Transport in Porous Media," Critical Reviews in Environmental Control, 19(1), 33-99, (1989).
22. Harmon, T. C., W. P. Ball, and P. V. Roberts, "Nonequilibrium Transport of Organic Contaminants in Groundwater," in Reactions and Movement of Organic Chemicals in Soils, B. L. Sawhney and K. Brown, eds., pp. 405-437, SSSA Special Publication Number 22, Soil Science Society of America and American Society of Agronomy, Madison, Wisconsin, 1989.
23. Bahr, J. M. and J. Rubin, "Direct Comparison of Kinetic and Local Equilibrium Formulations for Solute Transport Affected by Surface Reactions," Water Resources Research, 23, 438-452 (1987).
24. Jennings, A. A. and D. K. Kirkner, "Instantaneous Equilibrium Approximation Analysis," J. of Hydraulic Engineering, 110, 1700-1717 (1984).
25. Valocchi, A. J., "Validity of the Local Equilibrium Assumption for Modeling Sorbing Solute Transport Through Homogeneous Soils," Water Resources Research, 21, 808-820 (1985).
26. Cameron, D. R. and A. Klute, "Convective-Dispersive Solute Transport With a Combined Equilibrium and Kinetic Adsorption Model," Water Resources Research, 13, 183-188 (1977).
27. Wen, C. Y. and L. T. Fan, Models for Flow Systems and Chemical Reactors, pp. 68-208, Marcel Dekker, New York, 1975.
28. Chin, D. A., "Diagnostic Model of Dispersion in Porous Media," J. of Hydraulic Engineering, 115, 210-227 (1989).
29. Grisak, G. E. and J. F. Pickens, "Solute Transport Through Fractured Media 1. The Effect of Matrix Diffusion," Water Resources Research, 16, 719-730 (1980).
30. Grenney, W. J., C. L. Caupp, R. C. Sims, and T. E. Short, "A Mathematical Model for the Fate of Hazardous Substances in Soil: Model Description and Experimental Results," Hazardous Waste & Hazardous Materials, 3, 223-237 (1987).
31. Wu, J. C., L. T. Fan, and L. E. Erickson, "Modeling and Simulation of Bioremediation of Contaminated Soil," Environmental Progress, 9, 47-56 (1990).
32. van Genuchten, M. Th. and P. J. Wierenga, "Mass Transfer Studies in Sorbing Porous Media 1. Analytical Solutions," Soil Sci. Soc. Am. J., 40, 473-480 (1976).
33. Gvirtzman, H., N. Paldor, M. Magaritz, and Y. Bachmat, "Mass Exchange Between Mobile Freshwater and Immobile Saline Water in the Unsaturated Zone," Water Resources Research, 24, 1638-1644 (1988).
34. Rao, P. S. C., R. E. Jessup, D. E. Rolston, J. M. Davidson, and D. P. Kilcrease, "Experimental and Mathematical Description of Nonadsorbed Solute Transfer by Diffusion in Spherical Aggregates," Soil Sci. Soc. Am. J., 44, 684-688 (1980a).
35. Rao, P. S. C., D. E. Rolston, R. E. Jessup, and J. M. Davidson, "Solute Transport in Aggregated Porous Media: Theoretical and Experimental Evaluation," Soil Sci. Soc. Am. J., 44, 1139-1146 (1980b).
36. Crittenden, J. C., N. L. Hutzler, D. C. Geyer, J. L. Oravitz, and G. Friedman, "Transport of Organic Compounds with Saturated Groundwater Flow: Model Development and Parameter Sensitivity," Water Resources Research, 22, 271-284 (1986).
37. Goltz, M. N. and P. V. Roberts, "Three-Dimensional Solutions for Solute Transport in an Infinite Medium With Mobile and Immobile Zones," Water Resources Research, 22, 1139-1148 (1986).
38. Goltz, M. N. and P. V. Roberts, "Simulations of Physical Nonequilibrium Solute Transport Models: Application to a Large-Scale Field Experiment," J. of Contaminant Hydrol., 3, 37-63 (1988).
39. Roberts, P. V., and M. N. Goltz, R. S. Summers, J. C. Crittenden, and P. Nkedi-Kizza, "The Influence of Mass Transfer on Solute Transport in Column Experiments With an Aggregated Soil," J. of Contaminant Hydrol., 1, 375-393 (1987).
40. Fong, F. K. and L. A. Mulkey, "Simulation of Solute Transport in Aggregated Media," AICHE J., 35, 670-672 (1989).
41. Pellet, G L., "Longitudinal Dispersion, Intraparticle Diffusion, and Liquid-Phase Mass Transfer During Flow through Multiparticle System," Tappi, 49(2), 75-82 (1966).
42. Satterfield, C. N., C. K. Colton, and W. H. Pitcher, Jr., "Restricted Diffusion in Liquids Within Fine Pores," AICHE J., 19, 628-635 (1973).
43. Prasher, B. D. and Y. H. Ma, "Liquid Diffusion in Microporous Alumina Pellets," AICHE J., 23, 303-311 (1977).
44. Ball, W. P. and P. V. Roberts, "Slow Diffusion of Sorbing Hydrophobic Organic Compounds in Sandy Aquifer Material," in Preprints of Papers Presented at the 199th ACS National Meeting, 30(1), pp. 313-317, Boston, 1990.
45. Mackay, D. M. and J. A. Cherry, "Groundwater Contamination: Pump-and-Treat Remediation," Environ. Sci. Technol., 23, 630-636 (1989).
46. Wu, J. C., L. T. Fan, and L. E. Erickson, "Modeling of In Situ Neutralization and Biodegradation Processes," in Proceedings of the Conference on Hazardous Waste Research, L. E. Erickson, ed., pp. 35-48, Kansas State University, Manhattan, Kansas, 1988.
47. Janssen, L. P. B. M., J. Prins, A. C. Hoffmann, R. J. De Meijer, and A. W. L. Veen, "Modeling the Migration of Contaminants in Soil," Chem. Eng. Comm., 89, 37-47 (1990).
48. Pekdeger, A., "Pathogenic Bacteria and Viruses in the Unsaturated Zone," in Pollutants in Porous Media The Unsaturated Zone Between Soil Surface and Groundwater,

B. Yaron, G. Dagan, and J. Goldsmith, eds., pp. 195–206, Springer-Verlag, New York, 1984.

49. Borden, R. C. and P. B. Bedient, "Transport of Dissolved Hydrocarbons Influenced by Oxygen-Limited Biodegradation 1. Theoretical Development," Water Resources Research, 22, 1973–1982 (1986).

50. Molz, F. J., W. A. Widdowson, and L. D. Benefield, "Simulation of Microbial Growth Dynamics Coupled to Nutrient and Oxygen Transport in Porous Media," Water Resources Research, 22, 1207–1216 (1986).

51. Rifai, H. S., P. B. Bedient, J. T. Wilson, K. M. Miller, and J. M. Armstrong, "Biodegradation Modeling at Aviation Fuel Spill Site," J. of Environmental Engineering," 114, 1007–1029 (1988).

52. Widdowson, M. A., F. J. Molz, and L. B. Benefield, "A Numerical Transport Model for Oxygen-and Nitrate-Based Respiration Linked to Substrate and Nutrient Availability in Porous Media," Water Resources Research, 24, 1553–1565 (1988).

53. Baek, N. H., L. S. Clesceri, and N. L. Clesceri, "Modeling of Enhanced Biodegradation in Unsaturated Soil Zones," J. of Environmental Engineering, 115, 150–172 (1989).

54. Celia, M. A., J. S. Kindred, and I. Herrera, "Contaminant Transport and Biodegradation 1. A Numerical Model for Reactive Transport in Porous Media," Water Resources Research, 25, 1141–1148 (1989).

55. Scholze, R. J., Jr., E. D. Smith, J. T. Bandy, Y. C. Wu, and J. V. Basilico, eds., Biotechnology for Degradation of Toxic Chemicals in Hazardous Wastes, Noyes Data Corporation, New Jersey, 1988.

56. Sims, J. L., R. C. Sims, and J. E. Matthews, "Approach to Bioremediation of Contaminated Soil," Hazardous Waste & Hazardous Materials, 7, 117–149 (1990).

57. Rifai, H. S. and P. B. Bedient, "Comparison of Biodegradation Kinetics With an Instantaneous Reaction Model for Groundwater," Water Resources Research, 26, 637–645 (1990).

58. Kindred, J. S. and M. A. Celia, "Contaminant Transport and Biodegradation 2. Conceptual Model and Test Simulations," Water Resources Research, 25, 1149–1159 (1989).

59. Baveye, P. and A. Valocchi, "An Evaluation of Mathematical Models of the Transport of Biologically Reacting Solutes in Saturated Soils and Aquifers," Water Resources Research, 25, 1413–1421 (1989).

60. Characklis, W. G. and K. C. Marshall, Editors, Biofilms, pp. 707–732, Wiley, New York (1990).

61. Cunningham, A. B., E. J. Bouwer, and W. G. Charcklis, "Biofilm Accumulation in Porous Media," pp. 63–76, Proceedings of the Conference on Hazardous Waste Research, L. E. Erickson, Ed., Kansas State University, Manhattan, KS (1990).

62. Rasmuson, A., "The Effect of Particles of Variable Size, Shape and Properties on the Dynamics of Fixed Beds," Chemical Engineering Science, 40, 621–629 (1985).

63. Ghiorse, W. C. and D. L. Balkwill, "Enumeration and Morphological Characterization of Bacteria Indigenous to Subsurface Environments," Developments in Industrial Microbiology, 24, 213–224 (1983).

64. Wilson, J. T., J. F. McNabb, D. L. Balkwill, and W. C. Ghiorse, "Enumeration and Characterization of Bacteria Indigenous to a Shallow Water-Table Aquifer," Ground Water, 21, 134–141 (1983).

65. Bailey, J. E. and D. F. Ollis, Biochemical Engineering Fundamentals, 2nd Ed., pp. 373–456, McGraw-Hill, New York, 1986.

66. Sewell, G., "IMSL Software for Differential Equations in One Space Variable," IMSL Technical Report Series 8202 (1982).

67. Dhawan, S., L. E. Erickson, L. T. Fan, P. Tuitemwong, and R. Mahadevaiah, "Microcosm Techniques for Investigating the Biodegradation Potential of Light-Non Aqueous Phase Liquids and Dense-Non Aqueous Phase Liquids," pp. 578–599, Proceedings of the Conference on Hazardous Waste Research, L. E. Erickson, Ed., Kansas State University, Manhattan, KS (1989).

68. Lauffenburger, D. and B. Calcagno, P., "Competition Between Two Microbial Populations in a Nonmixed Environment: Effect of Cell Random Motility," Biotechnol. Bioeng., 23, 2103–2125 (1983).

69. Perry, R. H. and D. W. Green, Editors, Perry's Chemical Engineers' Handbook, p. 3–258, McGraw-Hill, New York (1984).

70. Johnson, M. J., "Aerobic Microbial Growth at Low Oxygen Concentration," J. Bacteriol. 94, 101–108 (1967).

71. Gray, T. R. G., and D. Parkinson, Editors, The Ecology of Soil Bacteria, p. 172, University of Toronto Press, Toronto, Ontario, Canada (1968).

72. Hausenbuiller, R. I., Soil Science, pp. 73–98, Brown Company Publishers, Dubuque, Iowa, (1978).

A Research Institute Wastewater Treatment Program

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A research institute, due to its routine use of chemicals, equipment, and energy in research activities, is without exception a waste generator. The Development Center for Biotechnology in Taiwan, the Republic of China, has therefore taken the initiative in constructing an up-to-date plant for the treatment of liquid wastes in consideration of the public concerns and environmental impact. From the start operation of the wastewater treatment plant in July, 1989, the effluent quality has been maintained, at one hundred percent of the time, lower than the effluent discharge limits. The gained operation experiences as well as qualitative and quantitative aspects of liquid waste outputs from the biotechnology research institute are presented.

INTRODUCTION

Research institutes including universities and specialty research centers of excellence, because of their utilization of a variety of chemical or biological materials, are producers of waste materials of environmental concerns. Due to their variety, though the amount is small compared to that of industrial wastes from manufacturing facilities, these wastes must be treated and discharged in a manner not similar to the operation of the later. As technology advances, a large number of wastes-producing institutions have been established. The U.S. Environmental Protection Agency (USEPA) has estimated that the total amount of hazardous wastes generated by research/educational institutions ranges from 2,000 to 4,000 metric tons per year in the United States [1].

Wastes generation at educational and research institutions differs from that of industrial manufacturing plants. Generally, educational and research institutions use a small amount of a wide variety of chemicals, as a result, the wastes generated are only small quantities of a wide diversity of materials instead of a large volume. The discharge of wastes from educational and research institutions, therefore, requires more efforts to the implementation of appropriate management strategies for these wastes [2].

For the past years, the Republic of China, prompted by the need of developing competitive novel chemical and biological products for the expanding local market as a result of its economic bloom, has intensified research activities. More and more public and private research centers have emerged and thus almost all kinds of wastes have been generated by these organizations. As pollution control regulations become more rigid, treatment solutions to these waste have attracted much attention from all parties. Waste generation from these research activities is by all respects identical to those mentioned above for similar research laboratories. To cope with the waste discharge problems, and also to encourage and enforce environmental protection measures, the Environmental Protection Administration in the R.O.C. has promulgated regulations which mandate educational and research institutions to comply with strict discharge standards.

Wastes produced by educational and research institutions exist in the liquid (aqueous), gas and solid states. Wastewaters produced from educational and research institutions are characteristic of low amount and high variety, and may incur severe toxicity and hazards to the environment. For quite a period of time, wastewaters from research institutions in the R.O.C. had not been adequately and sufficiently treated. Sometimes, direct dumping of wastes into the open sewer without treatment was the only mean, while such untreated wastes, through evaporation to air and leaching into the ground, may lead to a significant cause of environmental pollution.

Since its establishment in 1984, the Development Center for Biotechnology (DCB) has been actively conducting researches
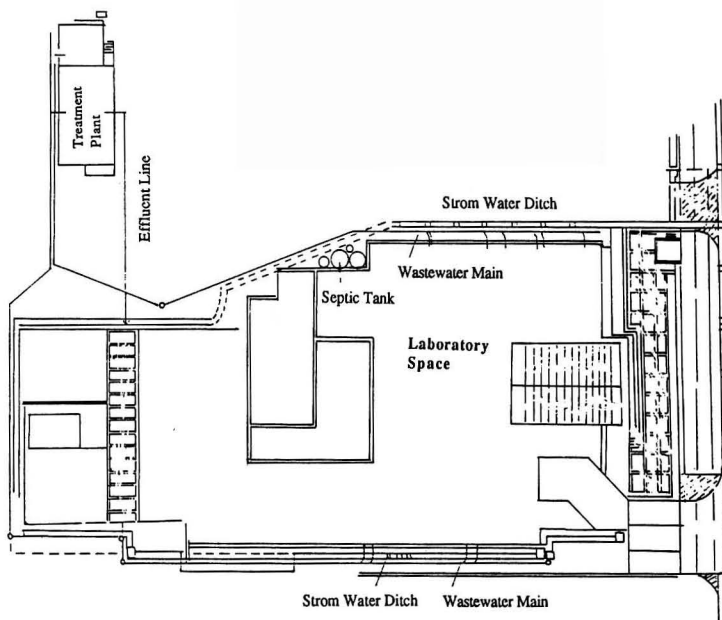
FIGURE 1. The Plan of DCB Laboratory Building and Layout of Wastewater Collection and Discharge Lines

on developing existing or novel bioproducts under the auspices of the R.O.C. government. The center includes microbiology and fermentation, wastewater treatment process research, agricultural biotechnology, molecular biology, biochemistry, applied chemistry, cell biology and immunology, and fermentation process development. The institute has the laboratory space of about 54,000 square feet and currently employs more than three-hundred scientists and engineers from all fields. To assure compliance with the regulations, the DCB has had to dispose of all wastes generated in a rightful manner before draining to the sewer. As the major source of waste discharge, the water wastes from laboratory sinks are collected and treated in a well-equipped wastewater treatment plant. The wastewater treatment plant is the first one built for ed-

ucational and research institutions in the city of Taipei, and since July of 1989, the plant has been operated successfully as designed.

In the following discussion, particular emphasis will be laid on liquid waste characteristics and the resulting treatment plant performance. The waste management program at DCB will also be briefly outlined.

WASTEWATER POLLUTION PREVENTION PRACTICES

The most distinct pollution discharge at DCB is the wastewater. In this section, wastewater generation and method

Table 1 Wastewater Discharges from the DCB Laboratories

Division (1)	Wastewater output	Volume discharged (L/day)	Remarks
Microbiology & Fermentation	Fermentation Broth	3	(2)
	Cooling Water, 8hr × 150L/hr	1,200	
	Wastewater Treatment Reactor effluent	2	(3)
	Laboratory Sinks, 1hr × 360L/hr	360	
	Central Cleaning, 4hr × 300L/hr	1,200	
Molecular Biology Biochemistry Cell Biology & Immunology	Laboratory Sinks, 0.5hr × 360L/hr	180 × 5	(2)
Applied Chemistry	Central Cleaning, 4hr × 300L/hr	1,200 × 5	
Agricultural Biotechnology	Cooling, general, 8hr × 100L/hr	800	
Total		10,465 L/day	

(1) Waste broth from the Fermentation Process Development Division is separately accounted for in Table 2.
(2) Organic solvents were collected and was contracted out for treatment by a hazardous waste treatment company (see text).
(3) Wastewater analysis residues (for example COD) were collected and treated by contractor assigned by the "Association of Wastewater Analytical Laboratory".

Table 2 Wastewater Discharge from Large Fermenters in the Fermentation Process Development Division

Fermenter Sizes	Number	Application Frequency	Wastewater Discharges	Discharge Quantity (L)	Wastewater Flowrate (L/month)
5L	1	0.5/month	cooling	1,500	753
			waste broth	5	
15L	1	0.5/month	cooling	2,000	1,007
			waste broth	15	
20L	3	2×1/month	cooling	2,500	5,040
			waste broth	20	
150L	2	2×1/month	cooling	9,600	19,350
			waste broth	70	
1,500L	1	0.5/month	cooling	10,000	5,750
			waste broth	1,500	
Total (per month)					31,901
Flowrate per day (L/day)					1,063

of treatment are described. The governing regulations is also introduced.

Research Laboratory Wastewater Regulations in the R.O.C.

A campaign launched in the year 1989, called "Project Nobel", was aimed at enforcing wastewater control for educational and research institutions in the R.O.C. Under this project, pollution problems because of wastes generated from educational and research institution laboratories should be corrected within the period between the 1st of July, 1989 and June 30, 1990. Wastewater pollution control under this project was legally regulated under the "Water Pollution Control Law." Under this law, each educational and research institution must establish its wastewater discharge point, and local environmental protection bodies are to sample wastewater discharge at random and test for the violation of the wastewater discharge limits. Waste constituents limited by the standards include itemized toxic organics and heavy metals. For example, the limiting values for Pb, Hg, Cr, and Cu are 1.0, 0.005, 0.1, and 3.0 mg/L, respectively. For the general wastewater characterizations such as COD, BOD, and SS, the limits are 300, 80 and 200 mg/L, respectively. In addition, the effluent should be a clear liquid as defined by a 15 cm of the "Visibility" test [3].

The Development Center for Biotechnology has taken a lead over all other educational and research institutions in the Taipei area in its ability to comply with the above regulations.

Wastewater Flowrate

Except for the sanitary wastewaters of kitchen and lavatory origins, wastewaters from laboratory bench sinks were collected by wastewater mains and discharged to a central wastewater treatment plant. The general layout of the DCB wastewater pipelines are illustrated in Figure 1.

The kind and amount of wastewater flows each day from different divisional laboratories at DCB are summarized in Table 1 and wastewater flows each month from the Fermentation Process Development division are separately listed in Table 2. The listed amount did not include any organic solvents which may be environmental hazardous and may impose undesirable effects on the biological treatment processes (see footnotes of Table 1). Organic solvents used in the biotechnology laboratory are mainly from the operations of electrophoresis, cell treatment buffers, and liquid chromatography. Under a detailed hazardous waste management program, these solvents were collected in the glass bottles and were sent to a hazardous waste treatment company for disposal by contract. The amount of hazardous organics collected at DCB, however, was usually less than one liter per month from each laboratory.

Wastewater flows into the treatment plant were continuously metered. The measured flowrates during the Spring season of 1990 averaged at 12 cubic meters per day (CMD). This amount of flow was approximately accountable from the 11 CMD as indicated in Tables 1 and 2. In addition, water supply was metered at 16 CMD during the same period of time. This amount, minus an approximated 6 CMD (300 persons at around
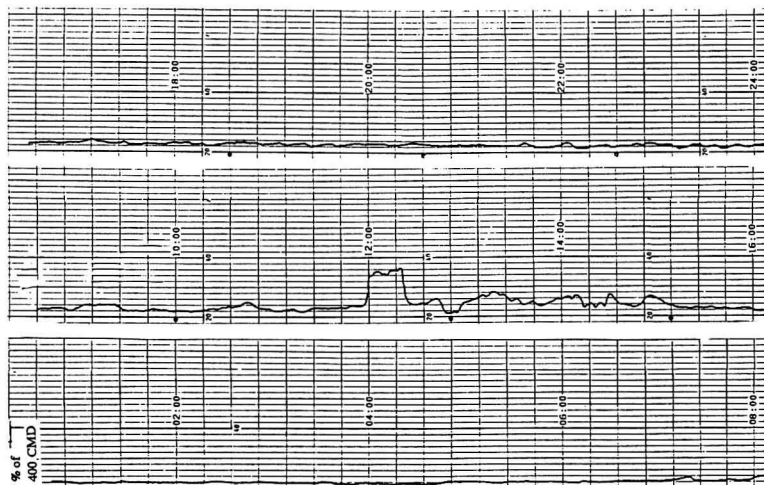

FIGURE 2. A Typical One-day Flow Pattern of Wastewater into the DCB Wastewater Treatment Plant
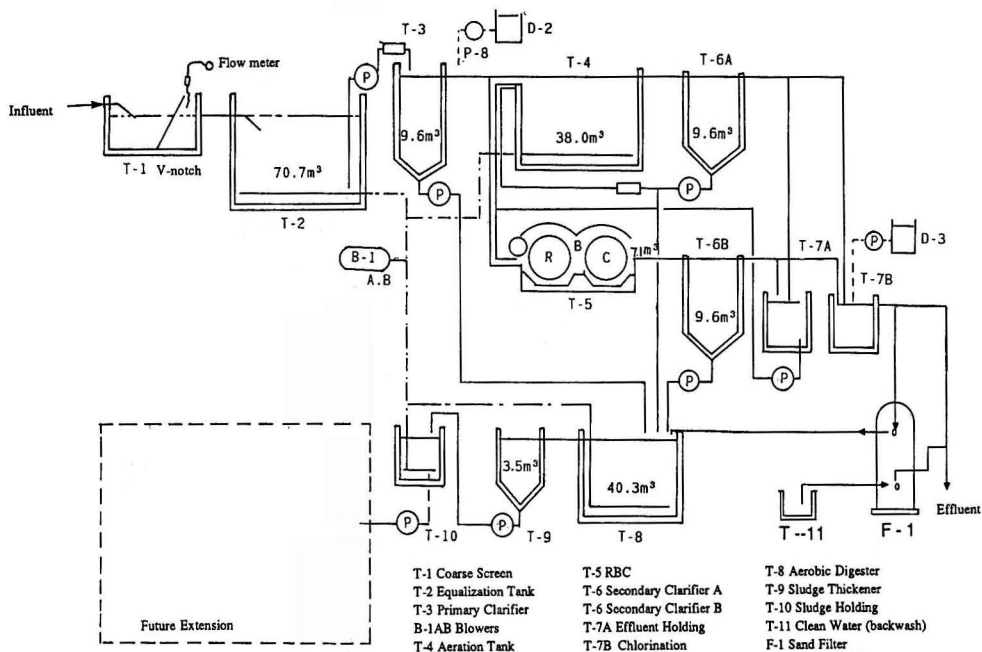
FIGURE 3. Flow Scheme of the DCB Wastewater Treatment Plant

T-1 Coarse Screen	T-5 RBC	T-8 Aerobic Digester
T-2 Equalization Tank	T-6 Secondary Clarifier A	T-9 Sludge Thickener
T-3 Primary Clarifier	T-6 Secondary Clarifier B	T-10 Sludge Holding
B-1AB Blowers	T-7A Effluent Holding	T-11 Clean Water (backwash)
T-4 Aeration Tank	T-7B Chlorination	F-1 Sand Filter

20 L per person per work day) sanitary uses, also indicates an approximate balance in the water use.

A typical wastewater flow as recorded by the flow meter during a work day (May 16, 1990) is shown in Figure 2. It can be observed that the flow into the treatment plant became intensified between 9 a.m. and 16 p.m. Flow during the night was minimal. A flow pattern like that in Figure 2 amounts to a total flow of 7.0 CMD.

Description: the DCB Wastewater Treatment Process

The central wastewater treatment plant at DCB is comprised of biological processes which are designed to meet the secondary treatment standards. An activated sludge process and a rotating biological contractor (RBC) are installed in parallel. Detailed layout of the whole plant is shown in Figure 3. Wastewaters coming from the mains pass through a fine screen into an equalization tank of 70 cubic meters. Before gravity flow into the equalization tank, wastewater is retained in a trough at which end a V-notch weir is installed. Wastewater level in the front of the weir is monitored using a sonar liquid level detector which translates the readings into flowrates. Wastewater in the equalization tank is mixed by aeration. From the equalization tank wastewater is pumped into a primary settling tank. The pumping time is automatically controlled by a water level sensor. From the primary settling tank, wastewater overflows in equal proportions into the parallel activated sludge and RBC tanks. Wastewater treatment then follows the general operations of activated sludge and RBC processes, from which excess sludge is pumped to an aerobic digestion tank. Effluents from the secondary clarifiers are converted in a holding tank and pressurized through a sand filter for polishing suspended solids (SS) which may at times produce clarity problem, resulting in violating the visibility standards. Finally, the effluent flow through the chlorination tank before

discharging into the designated discharge point is shown in Figure 2.

The excess sludge from both the activated sludge and the RBC is wasted into an aerobic digestion tank in which sludge is aerated for a prolonged period of time. Suspension from the digester is settled at a sludge thickener, from which the supernatant is returned to the equalization tank. Thickened sludge is periodically hauled away by truck.

The treatment plant is delicately built through good design and planning. Noise and other nuisance are well controlled. Such existence of a wastewater treatment plant in the urban city is esthetically acceptable.

TREATMENT PLANT OPERATION

The operation of the DCB wastewater treatment plant was conducted to meet wastewater discharge limits. The main operation control of the plant is centered on the activated sludge and RBC units. Because the influent flowrate and its COD were much lower than the designed values, probably the biological treatment units were not operated at the optimal conditions. Taking the activated sludge as an example, the low flowrate and low BOD together resulted in a very low mixed liquor suspended solid (MLSS) concentration. Process control using the rational mean cell residence time method, has made much of the time not feasible. Basically, simplicity is sought for in the plant operation, while maximizing MLSS retention. Because the flow from the equalization tank was automatically controlled, the hydraulic residence times of the activated sludge and RBC were controlled by the average daily flow rather than by a designated value. Secondary sludge of the activated sludge was returned to the aeration tank at about ninety five percent (95%) to increase MLSS. Small amount of RBC secondary sludge is returned whenever biofilm on RBC is observed low.
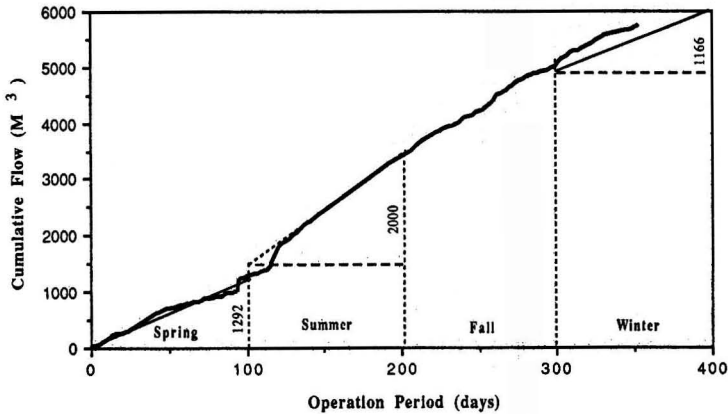
FIGURE 4. Cumulative Wastewater Flow at DCB during the Period of Spring and Winter in 1990

From the above mentioned sludge management, excess sludge to the digester is minimal. Following excessive aerobic digestion, mass of final sludge disposal is very low.

According to the above mentioned principle, the daily job of the plant operator included maintaining of proper machinery runs, meter reading, and sampling of wastewater for analyses at the analytical laboratory. Wastewater analyses were done mainly in COD. Sample-taking sites were installed at the points of influent before the screen, of activated sludge effluent from the secondary settling tank A, of RBC effluent from the secondary settling tank B, and of final effluent from discharge valve. Visibility of the effluent is measured whenever color or turbidity became abnormal. In addition, pH, SS, BOD, and heavy metal at various points were analyzed at irregular intervals.

Analyses of COD, BOD, S.S. and pH followed the guidelines provided by the Standard Methods [4]. Heavy metals were analyzed using atomic absorption spectrometry. Visibility test requires determination of the height of wastewater column through which a definite mark on a white disc at the column bottom can be seen when illuminated at 2000 Lux (lumen/m^2).

RESULTS AND DISCUSSION

The operation of the DCB wastewater treatment plant demonstrates the pollution correction measures carried out by a biotechnology research laboratory. In addition to providing the evidence of regulation compliance, results obtained from the operation are referable to the treatment plant design and operation required for similar research laboratories. Results generated during this period of operation, specifically about wastewater flowrate and pattern, wastewater quality, biological treatment efficiencies of this wastewater using activated sludge and RBC, and the efficiency comparison between these two processes, are discussed below.

During the period between 1990 and 1991, wastewater flowrate at DCB was considerably lower than the design value. Because of the lack of operation experience and of the reference data regarding the estimation of laboratory wastewater flowrate, particularly about those of a biotechnology laboratory where conducting of highly delicate experiments are required, the DCB wastewater treatment plant was obviously overdesigned by the environmental engineering consultants.

The cumulative wastewater flow at DCB for one year period is shown in Figure 4. It can be observed that wastewater flow at DCB exhibits a slight seasonal variation. During the spring or winter seasons, daily flowrate was at about 12 CMD, while a 20 CMD was found during the summer and fall. Based on the design flow of 80 CMD, the actual flow was only 15 to 20% at all times. This fact may have a dual effect on the biological units. First, the residence time in the equalization tank may extend to 3 to 4 days, resulting in a pause of flow to the biological treatment system. Evaporation loss from the basins sometimes occurred. Secondly, when the wastewater in the equalization tank reached the pumping level, full speed pumping created excessive surge to the treatment system. These disadvantageous effects were corrected by reducing the pump speed and adjusting the controlling wastewater level.

FIGURE 5. COD Influent and Combined Effluent of DCB Laboratory Wastewater

FIGURE 6. Comparisons of COD Treatment between Rotating Biological Contractor and Activated Sludge for DCB Laboratory Wastewater

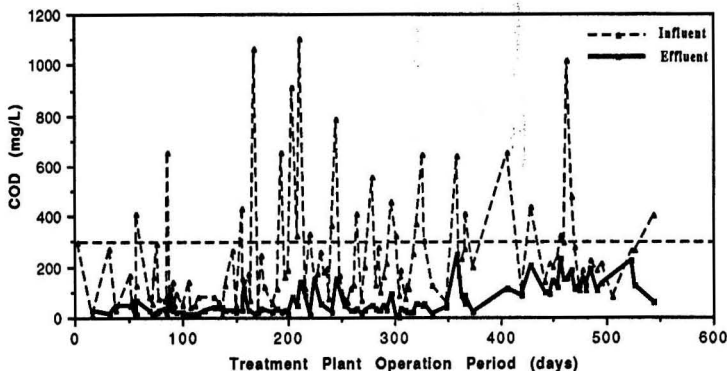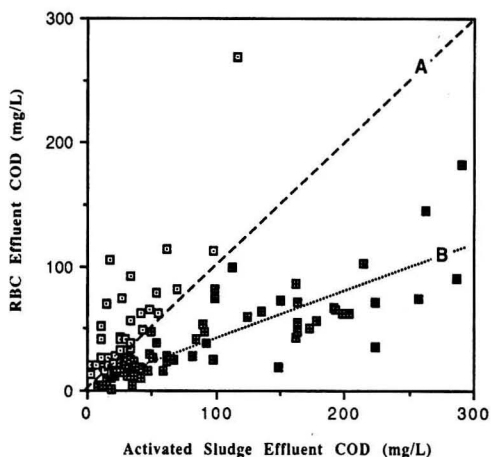Because of the recovery of organic solvent in advance (Table 1), the toxicity level of the DCB wastewater discharged to the treatment plant was low. Except for the waste fermentation broth which was sporadically discharged (see Table 2), sources of high wastewater COD were not common. The COD values of the influent wastewater and treatment effluent are listed in Figure 5. Fluctuation in the influent COD was observed, but seasonal variation was not obvious. The effluent wastewater quality was found at 100% of the time lower than the effluent limit of 300 mg/L. The long term low level of the influent COD, on the one hand, does not pose much of a treatment problem. Effluent quality is considered to be safe in the near future when effluent limits may become more stringent (for example, a COD limit of 200 mg/L is proposed for 1998). On the other hand, however, undesirable low biological growth occurs in the biological processes due to the underloading. Based on a 38 m³ activated sludge aeration tank volume, organic volumetric loading was calculated approximately 0.06 kg.COD/m³·day, which is about 90% lower than the lower recommended value of 0.6 kg.COD/m³·day for activated sludge.

The low organic loading is suspected to be one of the reasons for the sludge dispersion in the secondary clarifiers due to unsuccessful floc formation. This situation was observed particularly for RBC biomass. The RBC unit was evaluated using the EPA POTW Expert System (POTWEX) [5] and was found to be of marginal capacity mainly due to the negative scoring for under-loading hydraulically and organically. Although POTWEX utilizes municipal sewage as the main data base, it is able to indicate how the plant performance can be improved or its capacity can be fulfilled without prior modification.

Under the present loading situation, increase of organic wastes is advantageous to the operation of the existing treatment as designed. The input from the office sanitary wastewater to the plant is currently being investigated.

Two typical biological treatment processes, the activated sludge and RBC, were employed for the treatment of this laboratory wastewater. The original intention for employing these parallel systems was to provide an alternative which is more appropriate for the treatment of this wastewater of unknown characteristics. From the treatment results obtained over a period of more than one year, a comparison of the treatment performance between two processes was conducted. In Figure 6, the COD of effluent from RBC is plotted as a function of that of the activated sludge. Most of the data points

fall below line A, which represents the line of equal quality, indicating that RBC performance is better than that of activated sludge. By performing a regression analysis for these data, a slope of about 0.3 was found with line B as shown in Figure 6. According to the line B, the RBC performance can be as high as 3 times superior to that of activated sludge. For low BOD wastewaters, the fixed film process may produce more favorable treatment results than the suspended growth system. This result is valuable not only for academic researchers but also for practicing engineers who may find fixed film treatment system for the research laboratory wastewater treatment favorable.

The pH of the DCB wastewater is considered normal, at values between 7.1 to 7.5 at all times. The levels of heavy metals were found for $Pb < 0.1$ mg/L, $Hg < 0.001$ mg/L, $Cr < 0.1$ mg/L, and $Cu < 0.5$ mg/L. The BODs of the effluent were between 14 to 20 mg/L. These effluent qualities are able to meet effluent limits.

The MLSS at the aeration basin was found to be as low at 70 to 120 mg/L. The solids in the digester were found to be between 90 to 170 mg/L. At such a low MLSS level, and especially for the low growth of the RBC, the function of the secondary clarifiers was not pronounced. The effluent S.S., which at times might come up to 80 to 100 mg/L, created a turbidity problem. Although these S.S. values were allowed by the effluent limits, they might cause deterioration of effluent quality as regulated by the visibility test. To overcome the defect, a sand filtration effluent polishing unit was installed. Visibility problem was substantially corrected.

CONCLUSIONS

A research institute waste management program is successfully carried out with the significant reduction and recovery of hazardous wastes, while the major quantity of liquid waste is treated in a biological secondary treatment plant. The wastewater treatment plant is carefully operated and adjusted when necessary to produce effluent quality satisfactory to the regulated effluent limits. The wastewater flow volume and pattern, operation experience, and biological treatability of a research institute wastewater are very well exemplified.

ACKNOWLEDGMENTS

LITERATURE CITED

1. US Environmental Protection Agency, "Guides to Pollution Prevention: Research and Educational Institutions," Risk Reduction Engineering Laboratory, Cincinnati, OH, EPA/625/7-90/010 (1990).
2. Boortz, M. J., ,"Hazardous Waste Minimization and Management at an R & D Laboratory," *Environmental Progress*, 9, No. 1, p. 30 (1990).
3. Japan Industrial Standards, JIS No. K0102 (1986).
4. American Public Health Association, "Standard Methods for the Examination of Water and Wastewater," APHA, Washington, D.C., 16th ed. (1985).
5. US Environmental Protection Agency, "Handbook: Retrofitting POTWs," Center for Environmental Research Information, Cincinnati, OH, EPA/625/6-89/020 (1989).

NOx/CO Emissions and Control in Ethylene Plants

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The principal emission source of nitrogen oxides (NO_x) and carbon monoxide (CO) from ethylene plants is the pyrolysis furnace. This paper addresses NO_x/CO emissions and controls for gas fired pyrolysis furnaces. Typical NO_x and CO generation rates for furnaces are quantified. The impact of fuel composition on NO_x generation is discussed. Commercially available and emerging control technologies are reviewed. The relative costs of these controls are compared. Case-by-case considerations will dictate the selection of the control technology required to comply with the environmental demands of the specific site.

PYROLYSIS FURNACES

The use of a furnace with a tubular reactor to crack hydrocarbons in the presence of steam has been the commercially accepted method of producing ethylene for over 35 years. Different radiant coil designs featuring yield advantages and operating flexibility will require heat flux profiles tailored to optimize the reactor performance. Any integration of emission control features to the firebox which will alter or disturb this heat flux profile will be detrimental to the reactor performance.

During cracking operation, the reactor coil will foul with coke deposits. These coke deposits must be removed periodically to prevent the coil from exceeding its metallurgical temperature limit and to avoid excessive pressure drop. Coke removal is accomplished by removing the hydrocarbon feed and purging the coil with steam and a small amount of air for a period of about 12 to 48 hours to promote oxidation of the coke deposits. The firing rate is lower during this operation (approximately 30% of the normal firing rate) while the excess air value is higher (on the order of 150% versus 10% during normal operation). The flue gas temperature during the decoking operation is much lower than during normal operation.

NOx

Source, Generation, Causes, Contributing Factors

NO_x is produced in all external combustion processes using air. NO_x is produced primarily as nitric oxide (NO) in the hottest regions of the combustion zone. Some nitrogen dioxide (NO_2) is also formed, but its concentration amounts to 5 weight % or less of the total NO_x [1].

NO_x in combustion flue gas is derived from two mechanisms: thermal NO_x and fuel NO_x. Thermal NO_x is formed when the temperature in the combustion zone is high enough to cause thermal fixation of atmospheric nitrogen, which becomes significant above 1540 C (2800 F) [2]. Fuel NO_x is derived from the oxidation of free or bound nitrogen in the fuel.

The degree of combustion air preheat has an effect on NO_x emissions: NO_x emissions increase with increasing combustion air temperature. In one survey of fired heaters, NO_x emissions from a heater with 204 C (400 F) preheated combustion air were about 1.4 times higher than the NO_x emissions from the same heater on ambient combustion air [3].

There is an inverse relationship between NO_x and CO formation which plays an important role in emission control. In complete combustion, the carbon atoms in a hydrocarbon fuel are theoretically oxidized to carbon dioxide as in the simple equation:

$$C + O_2 \rightarrow CO_2$$
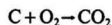
However, real world combustion processes do not perfectly bring together the three T's (time, temperature, and turbulence) to achieve complete combustion, and some amount of CO generation is inevitable. Generally speaking, the higher the peak combustion temperature, the lower the CO generation.

Unfortunately, the trend is just the reverse for NO_x generation; the higher the combustion temperature, the greater the NO_x generation [4]. Therefore, emission control for industrial combustion sources must be a compromise between NO_x and CO control.

Impact of Fuel Gas Composition on NO_x

Since the formation of NO_x depends on the combustion zone temperature, the composition of the fuel will strongly influence the emissions. For example, a fuel composed of 100% hydrogen will result in twice the NO_x formation as with a fuel with no hydrogen. This is due to higher flame temperatures with hydrogen rich fuels. The feedstock slate will determine the composition of the fuel gas and may also require firing some of the pyrolysis fuel oil, both of which will significantly affect the emissions.

A typical large scale modern ethylene facility will be capable of cracking a range of feedstocks from liquid feeds to gas feedstocks such as propane, butane, and ethane. Ethylene facilities are typically designed to operate continuously for 1 to 4 years between scheduled shutdowns for plant maintenance. During startup, natural gas or propane is normally imported for use as fuel. Once the facility is in operation, fuel gas will be produced as a by-product and will be partially or totally consumed by the pyrolysis furnaces, boilers, and other fired heaters within the facility.

Depending on the operation of the facility, this fuel gas will contain varying quantities of hydrogen. For example, on propane and butane feedstock the hydrogen content will be about 15 to 40 mole % and the unit will be a net exporter of fuel gas. On ethane feedstock the fuel gas will contain about 50 to 80 mole % hydrogen and there will be a small import of natural gas for fuel make-up. On liquid feedstocks the fuel gas hydrogen content may range from 5 to 10%.

The fuel gas by-products will range between 20 to 25% of the total products produced within the facility depending upon the feedstock. Because the fuel gas by-product has a low volumetric heating value relative to natural gas, it cannot be sold as a substitute for natural gas. Since it has no real market value, the fuel gas by-product must be consumed internally as fuel for the ethylene plant to operate economically. Consuming the fuel gas by-products within the facility has been accepted in ethylene plant economics and technology for over 25 years.

Additional equipment can be added to purify the fuel gas which will reduce the hydrogen content of the fuel gas. This equipment will separate some of the hydrogen from the fuel gas for export to other facilities. A reduction in NO_x emissions will result when burning purified fuel gas compared to fuel gas produced without the additional equipment for fuel gas purification. A 5 to 8% reduction in the NO_x emissions on all feedstock operating cases can be expected as a result of fuel gas purification.

Another environmental consideration is the nitrogen content of the make-up fuel. Nitrogen in the fuel is partially converted into NO_x upon combustion. Therefore, nitrogen content is an important consideration in the selection of alternative fuels.

Typical Generation Rate

Emissions from uncontrolled combustion sources are typically estimated using EPA's universal reference for air pollutant emission factors, AP-42 [5]. AP-42 does not specifically address process heaters. The AP-42 factor most often applied to fired heaters in the process industry is the factor for natural gas combustion in industrial boilers of 2.9 to 29 MW (10 to 100 MM BTU/hr) heat input, which is 2240 kg-NO_x/$10^6 m^3$ (140 lb-NO_x/$10^6 ft^3$) of fuel. Assuming the heat value of natural gas fuel is 8900 kcal/m^3 (1000 BTU/ft^3), this factor is equiv-

alent to 60.2 ng-NO_x/J (0.14 lb-NO_x/MM BTU) of firing duty. The heat specific form of the factor is conventionally used for emissions calculations.

Combustion Control: Burners

The pyrolysis furnace operates at relatively low excess combustion air levels (10% design, 5–20% in practice). Reducing NO_x emissions by further lowering excess air is not practical. However, combustion control by burner design is a NO_x control technique that has been successfully demonstrated on utility boilers and other stationary combustion sources.

So-called "low NO_x" burners have been successfully demonstrated and have earned industry acceptance. Favored low NO_x techniques include staging the combustion air and staging the fuel. Staged fuel is preferred over staged air as the low NO_x technique for gas fuel burners most widely adopted by burner vendors. Staged air is generally the accepted approach for liquid fuel burners. By minimizing the peak flame temperature and controlling the nitrogen-oxygen contact in the hottest zones, NO_x formation can be significantly reduced.

Early low NO_x burners were designed with staged combustion air to produce a primary combustion zone deficient in oxygen. This creates a primary combustion zone environment which is rich in reducing agents. The reduced partial pressure of oxygen tends to limit NO_x formation. A major disadvantage of the staged air burner is a loose undefined flame pattern, which is generally unacceptable for a high heat flux process heater. Staged air burners require considerably more space for mounting. Other options to produce staged air combustion (overfire air, burners out of service, biased firing) have been tried with varying success in utility boilers [6], but are generally unsuited to the practical operation of the pyrolysis furnace.

The most common low NO_x burner on the market today is the staged fuel burner. The technique of staged fuel combustion begins with combustion of a portion of the fuel with high excess air. The remainder of the fuel is injected in the second stage of the reaction and combustion is completed at low excess air. Burners designed for staged fuel combustion typically reduce NO_x emissions by about 25–40% compared to conventional burners, and even greater reductions are promised by the newer second generation low NO_x burners.

During the first stage, high excess air allows combustion to occur at a low flame temperature which inhibits thermal NO_x formation. As the combustion reaction goes to completion in the first zone, additional fuel is injected. The second reaction begins with a reduced partial pressure of oxygen which tends to limit the formation of NO_x.

Staged fuel burners can provide a flame pattern and shape which is compatible with the pyrolysis furnace requirements. Staged fuel burners have a history of successful installations in process heaters. Therefore, this technology has a proven track record and can be considered practicable.

The inherent drawback of any technique used to control NO_x emissions by lowering flame temperature is that CO emissions will increase. Using staged fuel burners, the CO concentration in the flue gas can be limited to about 50 ppmv. CO emissions of 50–100 ppmv are considered acceptable with combustion equipment designed for NO_x reduction [7].

Flue Gas Recirculation (FGR)

FGR uses a recirculated flue gas stream (normally about 10% of the total flow) for injection into the combustion zone or combustion air supply to reduce the flame temperature and oxygen concentration. FGR has not been fitted to a bottom-fired pyrolysis furnace and insufficient data exists to determine its effectiveness. FGR also decreases thermal efficiency, but recent research shows that the NO_x reduction potential can be impressive [8].

As with other NO_x reduction technologies, FGR lowers the flame temperature and lengthens the combustion zone, thereby tending to increase the amount of CO produced. Accordingly, the addition of FGR to a furnace may also require a CO abatement unit (discussed below) to reduce the attendant CO emissions to an acceptable level.

Implementing high ratios of FGR to the pyrolysis furnace would cause a significant altering of the heat flux profile to the cracking coil. As described earlier, the unique heat flux profile in the reactor coil is essential to pyrolysis furnace technology. FGR has not been applied to pyrolysis reactors and insufficient data is available to determine its effectiveness on this type of furnace.

Selective Catalytic Reduction (SCR)

SCR processes are based on the reaction of NO_x with ammonia in the presence of a catalyst, forming diatomic nitrogen and water vapor:

$$4 NO + 4 NH_3 + O_2 \rightarrow 4 N_2 + 6 H_2O$$

$$2 NO_2 + 4 NH_3 + O_2 \rightarrow 3 N_2 + 6 H_2O$$
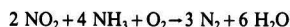
The SCR process requires a reactor, a catalyst, and an ammonia storage and injection system. In order for SCR to be effective, the flue gas temperatures must be maintained within a narrow reaction window which depends on the catalyst. Typical temperature windows for SCR catalysts range from 315 to 400 C (600 to 750 F), although a recent entry to the SCR market advertises a much broader temperature window of 165 to 370 C (325 to 700 F) [9].

SCR catalysts are commercially available in two types: base metal oxides (typically vanadium oxide and titanium oxide) and precious metal (typically platinum and rhodium). The base metal oxide catalysts can be bonded to a substrate (either ceramic or stainless steel) or dispersed in a homogeneous aluminosilicate zeolite. The precious metal catalysts are bonded to a stainless steel substrate. Base metal oxide catalyst SCR systems are now operating in Japan, Europe, and USA. The first commercial application of a precious metal SCR system is now operating in USA [10]. The precious metal SCR system advertises the benefit of oxidizing CO in addition to reducing NO_x [11].

Most of the demonstration work in SCR NO_x control can be found in the utility industry, and most of that activity is in Japan and Europe [12, 13]. The utility industry has cited the following concerns regarding the application of SCR to boilers: difficulty in matching the NH_3 injection pattern to the non-uniform flow of NO_x in the ductwork; inability to optimize NH_3 injection rate by feedback control; reliability of NH_3 monitors; catalyst deactivation by heavy metal poisoning; process control under load swings; and spent catalyst disposal [14].

In addition to the concerns voiced by the utility industry, the obvious difficulties associated with fitting a SCR unit to the pyrolysis furnace include: complete redesign and reconstruction of convection section, environmental impact of ammonia leakage, large capital investment requirement, increased operating costs, and operational risks. The installation of an SCR system can be expected to be accompanied by unanticipated problems with production operations.

An example of a potential operating problem is proper control of the flue gas temperature entering the SCR unit. The SCR must operate within a narrow temperature window for effective NO_x reduction to occur. Temperature excursions outside of the reaction range can result in ammonia slip to the environment, as well as thermal shock and poisoning of the catalyst which may require replacing the catalyst.

Maintaining operation of the furnace within the SCR's temperature window is difficult outside of the normal design op-

eration. During startup or turndown operation, the firing rates change, resulting in a different flue gas temperature profile through the entire furnace.

Large scale ethylene plants have multiple pyrolysis furnaces, typically 6 to 12. Is it better to install individual SCR units dedicated to each furnace or to duct the flue gas from all the furnaces to one common SCR unit? The economics of scale favor combining the flue gas from all the furnaces into a single SCR unit.

However, a serious technical problem with the hypothetical single SCR arrangement is proper control of the flue gas temperature. An arrangement acceptable for normal operation would not be acceptable for the decoke operation. The turndown firing conditions will reduce the flue gas temperatures by several hundred degrees which would disturb the SCR unit operation. During the decoking operation, the flue gas flow rate will also be reduced, changing the residence time in the SCR unit.

The direct cost considerations of SCR include: SCR catalyst bed, ammonia storage/injection system, ammonia feed control system, NO_x/ammonia monitors, larger I.D. fan and driver, ductwork, and possibly a grade-mounted stack. Indirect costs include: licensor fees, increased plot requirements, insurance and administration, and loss of revenue resulting from unscheduled downtime and lost ethylene production. Operating costs include: ammonia, catalyst replacement, flue gas reheat losses, electricity, steam, and operations/maintenance/supervisory personnel.

Ammonia breakthrough is an undesirable side effect of SCR. In practice, some amount of the injected NH_3 will always escape reaction with the NO_x. A small amount of ammonia slip (about 1 to 15 ppmv depending on the effectiveness of the SCR unit) will be emitted to the atmosphere.

Selective Non-Catalytic Reduction (SNR)

There are at least two competing technologies for reducing NO_x emissions by post-combustion non-catalytic methods (SNR): ammonia injection and urea injection. Both technologies use a reducing agent (ammonia or urea) to react with NO_x to form nitrogen and water. There is wide disparity in the literature on the NO_x reduction achievable with these systems [15, 16, 17, 18, 19]. The principal areas of concern are: ammonia breakthrough, side reactions, safety, reliability, performance during load changes, and corrosion and fouling of heat transfer surfaces.

Ammonia Injection: The ammonia injection SNR method was developed by Exxon and carries the trade name "THERMAL DeNO$_x$." THERMAL DeNO$_x$ uses ammonia to reduce the NO_x emissions based on the same principals and chemical reactions as the SCR process, except that a catalyst is not utilized. The desired chemical reaction is:

$$NO_x + NH_3 + O_2 \rightarrow N_2 + H_2O$$
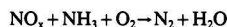
The absence of catalyst necessitates temperatures of 930 to 980 C (1700 to 1800 F) for the SNR reaction to take place. The reaction temperature can be extended down to 700 C (1300 F) by the injection of hydrogen along with the ammonia [20].

In addition to the desired NO_x reduction reactions, there are side reactions which take place at temperatures greater than 980 C (1800 F) that produce NO. Above 1090 C (2000 F), NO_x concentrations in the flue gas actually increase by the following reaction:

$$NH_3 + O_2 \rightarrow NO_x + H_2O$$
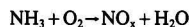
For these reasons, the injection of the ammonia into the furnace precisely at the point of desired temperature is critical [21]. This goal is difficult to achieve when the furnace load

changes and the firing rates of the burners vary with different feedstocks and run conditions. A properly designed ammonia injection system is essential to achieving the desired results.

The ammonia injection SNR process is further constrained by the fact that the absence of a catalyst slows the NO_x/NH_3 reaction. This extends the required retention time and narrows the temperature window for the reaction. These constraints require special design considerations of the convection section to accommodate an area where the ammonia can be injected at the proper flue gas temperature and with the required residence time.

Ammonia breakthrough is another undesirable side effect of the SNR process. In practice, some amount of the injected NH_3 will always escape reaction with the NO_x. EPA tested an industrial boiler equipped with THERMAL DeNO$_x$ and found that while the NO_x concentration in the flue gas was reduced by 41%, ammonia slip was 430 ppm [22].

Ammonia slip is a recognized environmental concern. A recent study funded by the California Air Resources Board modeled the effects of non-catalytic ammonia injection NO_x reduction from stationary combustion sources in the Los Angeles basin [23]. The study concluded that "use of noncatalytic ammonia injection technology for NO_x emission reduction has the potential to degrade NH_3 and aerosol nitrate air quality."

For the above stated technical reasons, the ammonia injection SNR method carries with it formidable engineering challenges in its application to the pyrolysis furnace.

Urea Injection: A competing SNR method uses urea as the reducing agent. "NO$_x$OUT" is the trade name for a post-combustion urea injection technology offered by Nalco Fuel Tech [24]. Noell, Inc. has recently introduced a "Two-Stage DeNO$_x$ Process" which injects urea and methanol in successive stages [25, 26]. To date, the bulk of the applications of the urea injection process has been in the utility industry on power generation boilers fired on coal and fuel oil [27].

In the urea injection SNR process, urea is injected into the combustion gas path. In the ensuing reaction, molecules of NO are converted to diatomic nitrogen and carbon dioxide. The desired chemical reaction is:

$$CO(NH_2)_2 + 2\,NO + 1/2\,O_2 \rightarrow 2\,N_2 + CO_2 + 2\,H_2O$$
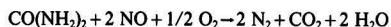
Urea + Nitric Oxide + Oxygen → Nitrogen
                              + Carbon Dioxide + Water Vapor

The above chemical reaction indicates that one mole of urea reacts with two moles of NO. However, greater-than-stoichiometric quantities of urea can be injected to improve NO_x reduction and to speed the reaction kinetics. This results in some ammonia slippage and a slight increase in CO; both are generated as by-products from the incomplete thermal decomposition of the excess urea [28].

While reducing NO, the injection of urea into the combustion path increases CO generation. In order to bring CO levels back down to acceptable levels, a catalytic CO abatement unit would be required. CO abatement units are discussed below.

The physical injection and mixing of the urea into the flue gas is essential to the process. The mechanics of injecting the urea solution to achieve proper distribution remains a developing art [29].

The licensor may require the addition of "enhancer chemicals" to the urea solution. If the licensor is the only supplier of these chemicals, some operators may find risk in relying on a sole supplier for chemicals which are needed on a daily basis.

The NO$_x$OUT process works best at temperatures above 870 C (1600 F) and below 1150 C (2100 F) [30]. This temperature range occurs near the bottom of the convection section of typical pyrolysis furnace designs and in the middle of one of the coils. While the convection coils could be reconfigured to accommodate a system of injectors, the flue gas temperature drops very fast at this point in the convection section, and residence time for the reduction reaction becomes a concern.

As with ammonia injection, the urea injection SNR process is a NO_x reduction technology which looks very promising. However, there are formidable technical problems which must be solved before it can be applied to pyrolysis furnaces.

Developing Technologies

There are other post-combustion technologies which are in developmental stages and will not be in commercial use for some time:

> electrogenerative reduction [31]
> electron beam radiation
> dry absorption by alkalized alumina [32]
> wet scrubbing [33]
> reburning [34]
> cyanuric acid injection [35]
> SO$_x$-NO$_x$-Rox Box [36]

R&D work in burner technology is very active. Surface combustion burners and burners combining steam injection, internal recirculation, and staged fuel are in the development stage and have already had limited field operations [37].

Costs

The costs of emission control systems play an essential role in determining what control system qualifies as Best Available Control Technology (BACT) [38, 39, 40]. In general, the trend for annualized cost of the control technologies described above runs as follows (from lowest cost to highest cost): low NO_x burners, FGR, SNR, SCR.

Actual costs per ton of NO_x removed will vary depending on site specific parameters (design removal %, utilities, labor, capital recovery, and other indirect costs). How these parameters influence costs can range enormously. For example, published sources have reported incremental removal costs for SCR vs. low NO_x burners (i.e., the difference in cost between SCR and low NO_x burners relative to the difference in NO_x removal) between $6000 and $12,000 per ton of NO_x removed [41, 42].

Carbon Monoxide

Typical Generation Rate

As with NO_x, CO emissions from combustion sources can be estimated from AP-42 [43]. The AP-42 factor most often quoted for CO is the factor for natural gas combustion in industrial boilers of 2.9 to 29 MW (10 to 100 MM BTU/hr) heat input, which is 560 kg-CO/10^6m^3 (35 lb-CO/10^6 ft^3) of fuel. Assuming the heat value of natural gas fuel is 8900 kcal/m^3 (1000 BTU/ft^3), this factor is equivalent to 15.1 ng-CO/J (0.035 lb-CO/MM BTU) of firing duty.

Catalytic Oxidation

This post combustion method uses an oxidation catalyst to convert CO to CO_2. The CO catalyst is typically a platinum group metal. Fitting a CO abatement unit to the pyrolysis furnace would involve:

a. Inserting a catalyst bed reactor in the convection section;
b. Redesigning the convection section to provide the temperature and residence time for the oxidation reaction; and
c. Installing a larger induced draft fan and driver.

The temperature range required for satisfactory operation of the CO unit is not as critical as with the SCR process.

Temperatures in the range of 260 to 650 C (500 to 1200 F) are acceptable depending on the catalyst substrate [44]. Catalyst life is expected to range from 3 to 5 years. Additional draft will be required to drive the flue gas through the CO oxidation unit. The increase in flue gas pressure drop demands a larger I.D. fan and driver. Where CO catalytic oxidation units are used in series with SCR units, the CO unit is placed upstream of the SCR unit to prevent oxidation of the SCR's ammonia to NO_x [45].

Combustion Control

As explained earlier, combustion equipment designed to minimize the formation of NO_x will produce increased levels of CO. The opposite is also true: burners designed to minimize CO will produce higher levels of NO_x. Therefore, there is a limit to the improvement available by controlling combustion temperature.

CO emissions can be minimized through the use of excess air trim of the combustion control system. The maximum thermal efficiency for the pyrolysis furnace is achieved at about 2% excess O_2 in the flue gas. Continuous O_2 and CO measurements can be used to operate the furnace at peak efficiency and low CO emission rates [46].

Costs

As noted with fitting SCR to the pyrolysis furnace, incorporating a CO oxidation unit would involve significant modifications to the convection section. Modifications to the convection coil layout and arrangement would introduce prohibitive costs for this technology. With NO_x reduction usually considered the higher environmental priority, CO control seems to be best achieved in terms of technology and cost effectiveness by combustion control.

SITE SPECIFIC REQUIREMENTS

Presently there are no federal New Source Performance Standards (NSPS) which would apply NO_x or CO generation limits to process heaters. Standards of performance for industrial-commercial-institutional steam generating units have been promulgated by EPA in the Code of Federal Regulations 40 CFR 60 Subpart Db. However, this NSPS specifically exempts process heaters [47]. Without an overriding NSPS, the selection of emission controls takes into account site specific considerations to meet environmental requirements. For example, the Texas Air Control Board (TACB) uses a three-tier approach to BACT based on precedent, technical practicability, and economic reasonableness [48].

The case-by-case nature of BACT is illustrated by a review of recent domestic ethylene projects. During the two year period 1988–1989, construction permits were approved for five major ethylene plants in Texas and Louisiana. Permit allowable NO_x emissions from the pyrolysis furnaces in these projects ranged from 34.4 to 97.6 ng-NO_x/J (0.08 to 0.227 lb-NO_x/MM BTU) of firing duty, and permitted CO emissions ranged from 15.1 to 29.7 ng-CO/J (0.035 to 0.069 lb-CO/MM BTU) [49]. Some state environmental control authorities are now calling for NO_x emission factors between 12.9 to 34.4 ng-NO_x/J (0.03 to 0.08 lb-NO_x/MM BTU), especially for ozone non-attainment areas.

Although we have discussed NO_x controls and CO controls individually, the selection of BACT for NO_x and CO is integrated. For example, it is plausible that a combination of lowering combustion temperature (which reduces NO_x but increases CO) and adding a CO catalytic oxidation unit may be more economical than installing an SCR to reduce NO_x.

SUMMARY

Commercially available and emerging NO_x and CO emission control technologies were reviewed to assess their applicability to the gas fired pyrolysis furnace.

Several technologies are now marketed for the control of NO_x from industrial combustion sources. The staged fuel low NO_x burner is the most commonly used technology for the management and control of NO_x generation from pyrolysis furnaces.

SCR technology is being used on commercial industrial furnaces with good results, but many difficulties remain in its application to pyrolysis furnaces, namely:
- complete redesign of convection section
- environmental impacts of ammonia leakage
- high capital and operating costs
- system control and monitoring

FGR has not been applied to pyrolysis furnaces as a NO_x emission control technology. However, historical data demonstrate the feasibility of FGR technology for small industrial furnaces. Additional testing and experience are required to tailor the technology to pyrolysis furnaces.

Emerging technologies such as SNR using ammonia or urea injection have been demonstrated on power generation boilers. SNR is a promising technology, but formidable engineering challenges exist in applying such emerging technologies to pyrolysis furnaces.

CO control in pyrolysis furnace flue gas is best achieved in terms of technology and cost effectiveness by combustion control. Although catalytic oxidation processes could be used, the capital costs are prohibitive.

The selection of control technologies for pyrolysis furnaces ultimately turns on what qualifies as Best Available Control Technology. BACT is a moving target which takes into account site specific requirements, regulations, precedent, technical practicability, and economic reasonableness.

LITERATURE CITED

1. *Compilation of Air Pollutant Emission Factors*, AP-42, Fourth Edition, Volume I, U.S. Environmental Protection Agency, Research Triangle Park, NC, p. 1.4-3 (September, 1985).
2. "Fired Heaters: Nitrogen Oxides Emissions and Controls," Report No. EPA/600/7-88/015, U.S. Environmental Protection Agency, Research Triangle Park, NC (1988).
3. Ibid.
4. *Fundamentals of Air Pollution*, Second Edition, Stern, A. C., Boubel, R. W., Turner, D. B., and Fox, D. L., "Sources of Air Pollution," Academic Press, pp. 82–86 (1984).
5. AP-42, op. cit., Table 1.4-1.
6. Bentley, K. M., and Jelinek, S. F., "NO_x Control Technology for Boilers Fired with Natural Gas or Oil," Tappi Journal, Vol. 72, No. 4, p. 123–130 (April, 1989).
7. Federal Register, Volume 51, No. 227, pp. 42783–42784 (November 25, 1986).
8. Napier, S., et al., "Low NO_x Burners for Stringent Emission Regulations," 1989 Fall International Symposium, American Flame Research Committee, International Flame Research Foundation (1989).
9. Samson, R., Goudriaan, F., Maaskant, O., and Gilmore, T., "The Design & Installation of a Low Temperature Catalytic NO_x Reduction System for Fired Heaters & Boilers," 1990 Meeting of the American Flame Research Committee, International Flame Research Foundation, San Francisco, CA (1990).

10. Stevens, R. L., Goff, J. L., and Thomas, A. H., "Santa Maria Cogeneration Project Selective Catalytic Reduction for NO_x Control," American Society of Mechanical Engineers, 1989 Joint Power Generation Conference and Exposition, Dallas, Texas (1989).
11. Pereira, C. J., Plumlee, K. W., Thomas, A. H., and Stevens, R. L., "Dual Function Catalyst System for Clean-Gas Applications," IGCI Forum '90, Air Pollution Controls for Energy Producing Facilities: Recent Operating Experience, Baltimore, Maryland (1990).
12. Sedman, C. B., and Ando, J., "Japanese Activities in SO_2 and NO_x Control," Energy Technology XV: Repowering America, Proceedings of the Energy Technology Conference, Government Institutes, Rockville, Maryland, pp. 179–193 (1988).
13. Cichanowicz, E., "Selective Catalytic Reduction Controls NO_x in Europe," Power Engineering, Vol. 92, No. 8, p. 36–38 (August, 1988).
14. Offen, G. R., Eskinazi, D., McElroy, M. W., and Maulbetsch, J. S., "Stationary Combustion NO_x Control," JAPCA, Vol. 37, No. 7, pp. 864–871 (July, 1987).
15. Castaldini, C., DeRosier, R., and Waterland, L. R., "Environmental Assessment of NH_3 Injection for an Industrial Package Boiler," Report No. EPA/600/7-86/005a, U.S. Environmental Protection Agency, Research Triangle Park, NC (February 1986).
16. Fellows, W. D., "Application of the Thermal DeNO$_x$ Process to Glass Melting Furnaces," 1989 Fall International Symposium, American Flame Research Committee, International Flame Research Foundation (1989).
17. Epperly, W. R., Broderick, R. G., and Peter-Hoblyn, J. D., "Control of Nitrogen Oxides Emissions from Stationary Sources," American Power Conference Annual Meeting (April 1988).
18. Heck, R. M., et al., Catalytic Air Pollution Controls: Commercial Development of Selective Catalytic Reduction for NO_x," Air Pollution Control Association Annual Meeting (1987).
19. Report No. EPA/600/7-88/015, op. cit.
20. Fellows, op. cit.
21. Haney, W. D., Siddiqi, A. A., and Tenini, J. W., "Controlling Nitrogen Oxides (NO_x)," 1983 National Petroleum Refiners Association Annual Meeting, Paper No. AM-83-30 (1983).
22. Castaldini, op. cit.
23. Russell, A. G., McCue, K. F., and Cass, G. R., "Mathematical Modeling of the Formation of Nitrogen-Containing Pollutants. 2. Evaluation of the Effect of Emission Controls," Environmental Science & Technology, Vol. 22, No. 11 (November 1988).
24. Epperly, op. cit.
25. Jones, D. G., et al., "Two-Stage DeNO$_x$ Process Test Data from Switzerland's Largest Incineration Plant," EPA/EPRI Symposium on Stationary Combustion NO_x Control, San Francisco, CA (March 1989).
26. Jones, D. G., Negrea, S., Lautenschlager, G., Rose, G., Smith, R. A., and Shiomoto, G. H., "Urea Injection NO_x Removal in European Coal-Fired Boilers and MSW Incineration Plants," 83rd Air & Waste Management Association Annual Meeting, Pittsburgh, PA (1990).
27. *Power*, "Developments to Watch," (August 1987).
28. Epperly, op. cit.
29. Epperly, op. cit.
30. Hofmann, J. E., "The NO$_x$OUT Process for Control of Nitrogen Oxides," NO_x Control Technologies and Methods—NO_x III, Council of Industrial Boiler Owners, Houston, Texas (February 1990).
31. Langer, S. H., et al., "Electrogenerative and Related Electrochemical Methods for NO_x and SO_x Control," Environmental Progress, Vol. 5, No. 4, pp. 277–282 (November 1986).
32. Haney, op. cit.
33. Tsai, S. S., Bedell, S. A., Kirby, L. H., and Zabcik, D. J., "Field Evaluation of Nitric Oxide Abatement with Ferrous Chelates," Environmental Progress, Vol. 8, No. 2 (May 1989).
34. Offen, op. cit.
35. Sarv, H., and Rodgers, L. W., "Evaluation of NO_x Control by Cyanuric Acid Injection in an Industrial-Scale Boiler," 1989 Fall International Symposium, American Flame Research Committee, International Flame Research Foundation (1989).
36. Chu, P., Downs, B., and Holmes, B., "Sorbent and Ammonia Injection at Economizer Temperatures Upstream of a High-Temperature Baghouse," Environmental Progress, Vol. 9, No. 3, pp. 149–155 (August 1990).
37. Khinkis, M. J., Kunc, W., and Xiong, T., "Experimental Evaluation of a High-Efficiency Surface Combustor-Heater Concept with Low Pollutant Emissions," 1989 Fall International Symposium, American Flame Research Committee, International Flame Research Foundation (1989).
38. 42 USC 7479(3).
39. 40 CFR 52.21(b)(12).
40. 31 TAC 116.3(a)(3).
41. Bentley, op. cit.
42. Offen, op. cit.
43. AP-42, op. cit., Table 1.4-1.
44. Chen, J. M., et al., "Commercial Development of Oxidation Catalyst for Gas Turbine Cogeneration Applications," 82nd Annual Meeting of the Air & Waste Management Association, Anaheim, California (1989).
45. Cobb, D., Glatch, L., Ruud, J., and Snyder, S., "Application of Selective Catalytic Reduction (SCR) Technology for NO_x Reduction from Refinery Combustion Sources," Environmental Progress, Vol. 10, No. 1, pp. 49–59 (February 1991).
46. Smith, E. P., "Considerations in Determining O_2 and CO Control for Combustion Efficiency and Quality," Industrial Heating, Vol. 54, No. 10, pp. 18–22 (October 1987).
47. 40 CFR 60.41b.
48. Horne, K., Mann, A., Neumann, K., and Seinfeld, J., "Control Technology," Texas Air Control Board Permits Workshop, Austin, Texas (November 1988).
49. McAngus, J. A., and Burnett, D. R., "Environmental Permitting of Ethylene Plants," American Institute of Chemical Engineers, Second Ethylene Producers Conference, Orlando, FL (March 1990).

Influence of Different Additives on the Reaction Between Hydrated Lime and Sulfur Dioxide

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Five commercial calcium hydroxides were tested in a fixed-bed reactor for SO_2 removal at bag-filter conditions. Small amounts of different additives (fly ash, NaOH, NaCl and $CaCl_2$) were added to the commercial $Ca(OH)_2$ which showed the greatest reactivity respect to SO_2 (by a drying process). Fly ash performance was negative whereas the rest of additives enhanced the desulfurization power of the $Ca(OH)_2$, specially NaOH (due to its basic and deliquescent character) and $CaCl_2$ (by its delilquescence). $CaCl_2$ has been the best additive tested at the used experimental conditions.

INTRODUCTION

The emissions of SO_2 is one of the great problems that leads to no desirable changes in our environment.

Nowadays, post-furnace injection of calcium hydroxide at low temperatures are probably the best process to apply for coal-fired utility stations, not only from a technical point of view but also from economical ones (in front of other processes like the wet process). The capital requirement is particularly low because the ductwork downstream of the air preheater and upstream of the particulate collection system (baghouse or ESP) provides the necessary reaction space for SO_2 capture.

Conoco Coal Research Division, the research arm of Consolidation Company, has developed one retrofit SO_2 control technology called Coolside. It consists of dry $Ca(OH)_2$ injection and flue gas humidification downstream of the air preheater [1, 2, 3, 4, 5].

Coolside removal of SO_2 can be increased by means of adding some substance (additive) dissolved into the humidification-water [4, 6, 7, 8, 9, 10, 11].

These additives can have one or two functions depending on its nature:

a.—Enhancing the reactivity of $Ca(OH)_2$ on reacting with SO_2.

b.—Acting as a SO_2 sorbent like $Ca(OH)_2$.

Ruiz-Alsop and Rochelle [8] have tested three different groups of additives:

— buffer acids (adipic and glycolic acids).
— organic deliquescents (ethylene glycol (EG), triethylene-glycol (TEG), and mono-ethanolamine (MEA)).
— inorganic deliquescents ($NaSO_4$, $NaSO_3$, $CaCl_2$, NaCl, $Ca(NO_3)_2$, $Co(NO_3)_2$, $NaNO_3$, $NaNO_2$, $BaCl_2$, $Na_2S_2O_3$, KCl, NaBr, LiCl).

They found that the deliquescent inorganic salts were the only substances that increase the $Ca(OH)_2$ reactivity. In order to explain those facts it is worth noting that the relative humidity is a very important variable because water plays an important role in the SO_2 capture. These deliquescent substances improve the $Ca(OH)_2$ reactivity [8] on achieving a great amount of water on the sorbent surface.

As a consequence, all of the substances that modify the moisture content of the $Ca(OH)_2$ solids in equilibrium with a gas phase of a given relative humidity would then be expected to change the reactivity of $Ca(OH)_2$ towards SO_2 [8].

Some additives in addition to having deliquescent properties can also act as co-sorbents respect to SO_2 like NaOH, $NaHCO_3$ and $NaCO_3$ due its alkalinity [4, 7, 9, 11, 13, 18].

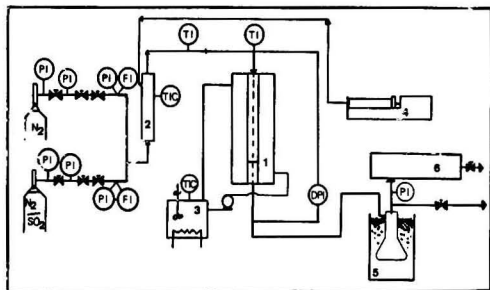Previous workers have reported NaOH performance widely [4, 6, 7, 11]. NaOH solution injection enhances the SO_2 re-

FIGURE 1. Apparatus for desulfurization tests: 1. Reactor; 2. Vaporizer; 3. Thermostatic bath; 4. Syringe pump; 5. Ice trap; 6. SO₂ analyzer.

moval and the Ca(OH)₂ utilization. It has got the two additive functions above mentioned.

Coolside 1 MW pilot tests data showed that SO_2 removal and sorbent utilization increased significantly when NaOH is injected with the humidification water. Total SO_2 removal (humidifier + baghouse) was increased from 50% with no additive to 85% with the additive at 0.1 NaOH/Ca(OH)₂ weight ratio, 13–14 °C approach to adiabatic saturation and mol ratio Ca/S = 2. The increment in SO_2 removal was significantly greater with the NaOH injection than the stoichiometric amount of SO_2 captured by the injected NaOH in the NaSO₃ and NaSO₄ form [11].

Bench-scale studies showed that Na_2CO_3 is as effective as NaOH but Na_2CO_3 has a lower cost [6]. Nevertheless, in the absorption process produced in the ductwork NaOH will be a better sorbent than Na_2CO_3 due to its major alkalinity.

The present paper describes the performance of five commercial calcium hydroxides, and the effect of additives for the SO_2 capture, and tries to correlate the additive water adsorption power with the increment of Ca(OH)₂ utilization and SO_2 removal.

EXPERIMENTAL

Apparatus

Experiments were conducted in the apparatus shown in Figure 1. The glass reactor, a jacketed Pyrex tube (12 mm in diameter, 450 mm in height) with a porous plate to hold 1.5 g of reactive solid diluted with 7.42 g of stainless steel coils (2 mm in diameter) to prevent channeling and an excessive pressure drop, was thermostated by pumping a thermic fluid (oil) from a external thermostatic bath. Simulated flue gas was obtained by mixing nitrogen and nitrogen/sulfur dioxide from cylinders. The flow of gas was monitored using microregulation valves and orifice meters. Water was metered by a syringe
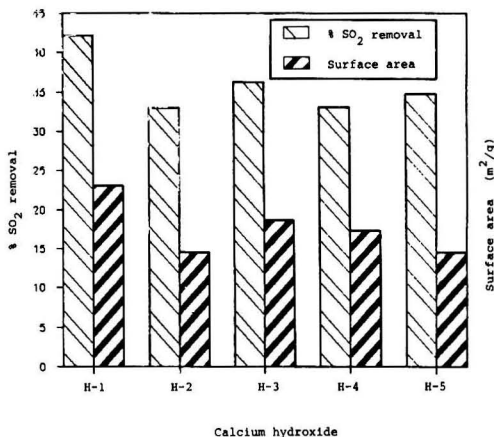

Calcium hydroxide

FIGURE 2. Comparison between SO₂ removal and specific surface of the five commercial calcium hydroxides. The same ordinate scale is used for both variables.

pump and evaporated in the vaporizer with the nitrogen/sulfur dioxide mixture.

Before entering the analyzer, the gas was cooled and water condensed by an ice trap. The SO_2 concentration was continously measured with a no dispersive infrared photometer UNOR 6N during the test which allows to have a ppm of SO_2 versus time curve. Each run was exactly repeated but reactive solid substituted for inert silica. The amount of SO_2 removal was calculated from the area enclosed by the two curves.

Sample Preparation

The sample preparation consisted of hydration of Ca(OH)₂ or Ca(OH)₂/fly ash placing 2 g in a filtering plate connected at a vacuum pump, adding water at 80°C with a weight ratio water/solid of 5 (this method tries to simulate the water pulverization in the wet process). The time of filtering was 15–25 s. The solid hydrated was rapidly introduced in a microwave oven (2,450 MHz) during 20 min for drying. Fly ash comes from Cercs (Barcelona) Power Station belonging to FECSA.

The mixtures Ca(OH)₂-additive were prepared adding the solid additive to Ca(OH)₂ previously hydrated and dried.

Desulfurization Conditions

Experiments were performed at temperature of 80°C and relative humidity of 60%. Flow rate gas in the reactor was 20

Table 1 Composition of the Five Commercial Hydroxides and Fly Ash

SOLID		CALCIUM HYDROXIDE Ca(OH)₂	CALCITE CaCO₃	LIME CaO	ANHYDRITE CaSO₄	QUARTZ SiO₂
Construction hydrated lime CIARIES S.A.	(Hydroxide-1)	85.0	11.5	1.5	2.0	—
Hydrated lime CIARIES S.A.	(Hydroxide-2)	91.5	6.6	—	2.0	—
Hydrated lime CALES DE PACHS S.A.	(Hydroxide-3)	100.0	—	—	—	—
Hydrated lime DECSA A Type	(Hydroxide-4)	89.8	6.7	3.5	—	—
Hydrated lime DECSA B Type	(Hydroxide-5)	86.5	8.6	3.0	1.9	—
Fly ash		—	—	7.0	8.0	5.0

Table 2 Desulfurization Using Dry and Hydrated Calcium Hydroxides			
SOLID	% SO$_2$ REMOVAL HYDRAT.	% SO$_2$ REMOVAL DRY	% INCREMENT
Hydroxide-1	57	42	36
Hydroxide-3	50	36	39

cm^3/s (80°C, 1.1 atm) and the concentration of SO$_2$ was 2,500 ppm. Experiments were run during 1.5 h.

Sample Characterization

The composition of the particles of the five Ca(OH)$_2$ and fly ash were found (see Table I) using a Rigaku S-Max/E X-ray fluorescence spectrometer. The surface area was measured using a sorbtometer Micromeritics Accusorb 2100-E.

RESULTS AND DISCUSSION

Desulfurization With Commercial Calcium Hydroxides

Desulfurization experiments carried out with the five commercial unhydrated calcium hydroxides showed (see Figure 2) that there was a correlation between SO$_2$ removal and surface area of the solid. The highest SO$_2$ removal was achieved when the solid with the highest surface area is used.

All of the hydroxides have a similar Ca(OH)$_2$ purity, so it can be inferred that surface area is an important parameter in the calcium hydroxide reactivity respect to SO$_2$ [12].

Afterwards two experiments were carried out using the two calcium hydroxides that shown the highest SO$_2$ capture (hydroxide 1 and 3) but they were previously hydrated as before described. The results of SO$_2$ removal by hydrated calcium hydroxides are shown in Table 2; as can be seen there is an strong increment in the percentage of SO$_2$ capture when the solids are hydrated before the desulfurization.

In both of dry and hydrated conditions hydroxide 1 removed the highest amount of SO$_2$, in such a way that it has been chosen to study the influence of four different additives (fly ash, NaOH, NaCl and CaCl$_2$) on its desulfurization power.
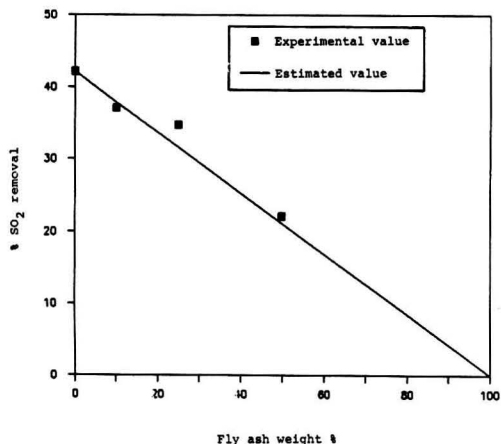
FIGURE 4. Estimated and experimental values of SO$_2$ removal by hydrated Ca(OH)$_2$/fly ash mixtures.

Desulfurization with Hydroxide 1-Fly Ash Mixtures

Three hydroxide 1-fly ash mixtures were prepared with weight percentages of 50, 75 and 90. Figure 3 shows the estimated and experimental percentages of SO$_2$ removal vs. fly ash percentage in the mixture. Estimated percentage was obtained by multiplying the solid percentage of SO$_2$ removal, as if the solid was Ca(OH)$_2$ only, by its weight percentage in the mixture and assuming that fly ash is an inert at this conditions. As can be seen estimated and experimental results roughly agreed, therefore fly ash can be considered as an inert solid and the SO$_2$ removal was only due to hydroxide 1.

FIGURE 3. Estimated and experimental values of SO$_2$ removal by dry Ca(OH)$_2$/fly ash mixtures.

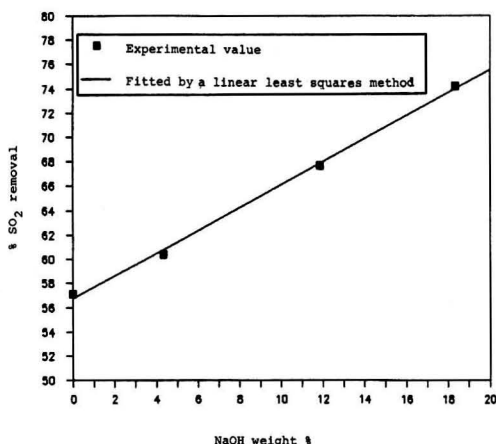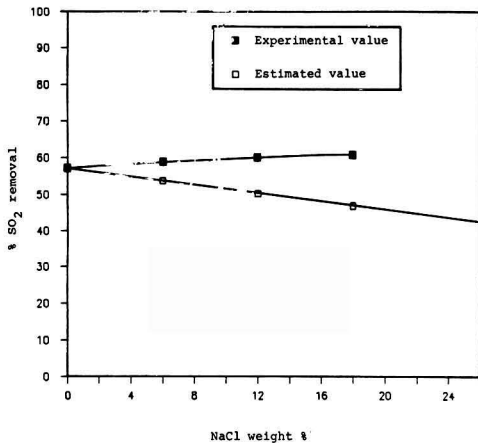FIGURE 5. SO$_2$ removal by hydrated Ca(OH)$_2$/NaOH mixtures.

FIGURE 6. Estimated and experimental values of SO_2 removal by hydrated $Ca(OH)_2/NaCl$ mixtures.
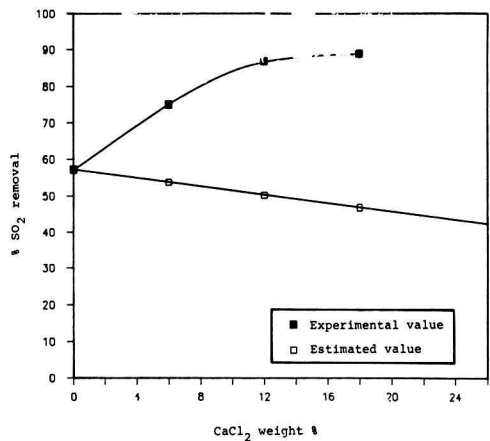

FIGURE 7. Estimated and experimental values of SO_2 removal by hydrated $Ca(OH)_2/CaCl_2$ mixtures.

Table 3 Specific Surfaces and SO_2 Removal Percentage of Mixtures Hydroxide-1 + 18% weight of additive

ADDITIVE	SURFACE AREA (m^2/g)	% SO_2 REMOVAL
NaOH	18	74
NaCl	14	61
CaCl$_2$	11	89

The three mixtures above described were hydrated before the desulfurization experiments. Experimental results (see Figure 4) suggest that SO_2 removal decreases as fly ash weight percentage increases but more strongly than when the mixture was not hydrated. One additional experiment was carried out using fly ash previously hydrated giving a SO_2 removal of 2%.

It can be concluded that fly ash (with a significant percentage of free calcium) do not improve the $Ca(OH)_2$ desulfurization power, even though the mixture was hydrated. In this case fly ash decreases the $Ca(OH)_2$ utilization, having a negative effect.

Desulfurization With Hydroxide 1—Additives Mixtures

These solids were prepared by mixing hydroxide 1 (perviously hydrated) with three percentages of additives (NaOH, NaCl and CaCl$_2$) in solid form.

Figure 5 shows the NaOH weight percentage (4, 12, 18%) influence on SO_2 removal. SO_2 capture correlates linearly with the amount of solid mixture. Basicity and hygroscopic character of NaOH are the variables that improve the SO_2 capture by $Ca(OH)_2$. Basicity achieves the SO_2 neutralization of gaseous phase and the hygroscopic character (deliquescent) modifies the $Ca(OH)_2$ moisture content and thus it increases the water amount on $Ca(OH)_2$ and supplies the SO_2 dissolution.

Three proportions of NaCl (6, 12 and 18%) were assayed as additive. Figure 6 shows the experimental results of this additive. The estimated values were calculated assuming that NaCl was an inert solid. By comparing experimental values to estimated ones it can be seen that the first values are higher than the second. So NaCl improved SO_2 capture by $Ca(OH)_2$ due to its deliquescent character [7, 8, 9, 13, 14, 15, 16, 17]. As mentioned, NaCl captures small amounts of moisture from the gaseous phase that increases the presence of SO_2 in dissolution and as a consequence its reactivity respect to $Ca(OH)_2$ is enhanced.

The three mixtures practically achieve the same percentage of SO_2 removal regardless of the amount of NaCl in the solid. This fact can be explained arguing that when the NaCl amount increases there are less $Ca(OH)_2$ left to capture SO_2, but the deliquescence of the solid is greater. So, both factors are counterbalanced. Therefore the deliquescence of one additive is a very important factor to improve the desulfurization power of $Ca(OH)_2$.

$CaCl_2$ as an additive was assayed at the same proportions than NaCl. Figure 7 shows the experimental and estimated results. This additive has a positive effect on the desulfurization power of $Ca(OH)_2$ too [3, 7, 8, 9, 10, 13, 14, 15, 16, 17, 18]. From the comparison of Figures 5, 6 and 7 it can be inferred that for the same percentage of additive $CaCl_2$ is the best of the three studied. Moreover, the differences between both experimental and estimated results are greater than in the case of NaCl.

It could also be deduced that at very high percentages of NaCl or $CaCl_2$ the SO_2 capture value decreased because their desulfurization power is practically zero. This tendency begins to be seen in Figure 7, $CaCl_2$ percentages of 12 and 18 do not practically increase the SO_2 removal (87 and 89% respectively).

Table 3 shows surface areas of three mixtures of hydrated hydroxide 1 and 18% weight of additive (NaOH, NaCl and CaCl$_2$). No correlation between the surface area and SO_2 removal has been found. The hydrated hydroxide 1-CaCl$_2$ mixture, which has the lowest specific surface, achieves the best SO_2 capture.

All of these results indicate that of the three main factors which increase SO_2 removal, namely, surface area, basicity and deliquescence, the last one has the greatest influence; in liquid phase the SO_2 removal is higher than in gaseous phase.

CONCLUSIONS

Five commercial calcium hydroxides were tested and the highest SO_2 removal was carried out by the hydroxide with the greatest surface area.

Calcium hydroxide hydration at atmospheric pressure increases its SO_2 removal power.

Mixing and hydration of mixtures $Ca(OH)_2$-fly ash produces a solid whose SO_2 retention is lower than $Ca(OH)_2$ alone. Therefore, at these used hydration conditions, the use of this combustion waste is inadvisable.

The SO_2 removal is increased linearly by adding NaOH to $Ca(OH)_2$ up to 18 weight %.

NaCl increases lightly the SO_2 removal and in the range of concentrations studied the mixtures gave practically the same desulfurization power.

$CaCl_2$ increases strongly these SO_2 removal. It was the best additive tested, because of its great deliquescent power which in the conditions explored is stronger than the basicity and specific area.

ACKNOWLEDGEMENTS

LITERATURE CITED

1. Yoon, H., F. W. Theodore, F. P. Burke, B. J. Koch, W. C. Corder, "Low Capital Cost, Reprofit SO_2 Control Technologies for High Sulfur Coal Applications," 79th. Annual Meeting and Exhibition "Air Pollution Control Association," Minneapolis (June 22–27, 1986).
2. Statnick, R. M., F. P. Burke, B. J. Koch, D. C. McCoy, H. Yoon, "Status of Flue Gas Sorbent Injection Technologies," 4th. Annual Pittsburgh Coal Conference (September 28, 1987).
3. Yoon, H., N. R. Stouffer, W. A. Rosenhoover, R. M. Statnick, "Laboratory and Field Development of Coolside SO_2 Abatement Technology," Proceedings, Second Pittsburg Coal Conference (September 16, 1985).
4. Yoon, H., P. A. Ring, F. P. Burker, "Coolside SO_2 Abatement Technology: 1 Mw. Field Tests," Proceedings, Coal Technology Conference, Pittsburgh (November 12, 1985).
5. Conoco, Technical Bulletin, "Coolside SO_2 Abatement Technology," (1985).
6. Stouffer, M. F., "Boiler Limestone Injection and Coolside Desulfurization Field Tests," Technical Committee Meeting Council and Industrial Boiler Owners (1986).
7. Yoon, H., J. A. Withum, W. A. Rosenhoover, F. P. Burke, "Sorbent Improvement and Computer Modeling Studies for Coolside Desulfurization," EPA/EPRI Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies (1986).
8. Ruiz-Alsop, R. N., G. T. Rochelle, "Fossil Fuels Utilization: Environmental Concerns," 209-222, Am. Chem. Soc., (1986).
9. Stouffer, M. F., H. Yoon, F. P. Burker, "The Mechanism of CaO Sulfation in Boiler Limestone Injection," 194th American Chemical Society National Meeting, August 30, New Orleans (1987).
10. Seeker, W. R., S. L. Chen, J. C. Kramlich, S. B. Greene, B. J. Overmoe, "Fundamental Studies of Low-Temperature Sulphur Capture by Dry Calcitic Sorbent Injection," Energ. Environ. Res. Corp., California Paper ID 6D.
11. Yoon, H., M. F. Stouffer, W. A. Rosenhoover, J. A. Withum, F. P. Burke, Environ. Progr., 7(2) (1988).
12. Jozewicz, W., J. C. S. Chang, Environ. Sci. Technol., 21, 664–670 (1987).
13. Staudinger, G., H. Schröfelbauer, H. Meier, "Laboratory Tests on Furnace Limestone Injection and Development of a Second Desulfurization Step with Fly Ash through Duct Injection," Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies (June 2–6, 1986).
14. Chang, C. S., G. T. Rochelle, A.I.Ch.E. J., 28(2), 261–66 (1982).
15. Rochelle, G. T., "Buffer Additives for Limestone Scrubbing: A Review of R & D Results," EPA/EPRI Symposium of Flue Gas Desulfurization, Hollywood (1982).
16. Spink, D. R., CHEMTECH, 364–69, June (1988).
17. Stouffer, M. F., H. Yoon, "Laboratory Calcination and Sulfation Studies for Boiler Limestone Injection," 6th International Workshop on Coal-Liquid and Alternative Fuels Technologies, Nova Scotia (September, 1986).
18. Bjerle, I., J. Klinspor, H. T. Karlsson, Ind. Environ. Protec., 4(1) (1984).

Recovery of Gallium and Arsenic from GaAs Wafer Manufacturing Slurries

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Lapping and polishing slurries from the gallium arsenide (GaAs) wafer manufacturing process were used to develop simple and inexpensive methods for separation and recovery of valuable gallium and toxic arsenic. The lapping slurry, containing GaAs, glycerol, alumina, iron oxide, and water, is treated by a process involving water addition, dissolution of GaAs, mixing, sedimentation, decantation, and evaporation. The polishing slurry, containing GaAs, silica, sodium bicarbonate, sodium hypochlorite and water, is treated simply by a repetitive cycle of adding water, mixing, settling, decanting, and evaporating. After treatment, the slurries contain less than 5 ppm of dissolved arsenic and are considered non-hazardous.

INTRODUCTION

As a semiconductor material, gallium arsenide exhibits certain advantages over silicon. The high electron mobility and semi-insulating properties of GaAs increase electrical performance and lower the power consumption of semiconductor devices. GaAs semiconductors have been widely used in light-emitting diodes, as well as microwave and digital integrated circuits, and their production is expected to continue to increase.

The manufacturing process for GaAs devices generates a substantial volume of waste containing arsenic solids, which is currently disposed in a Class I hazardous landfill. Arsenic is one of the several common elements designated as priority pollutants by the U.S. Environmental Protection Agency (EPA). Bowen reported that 0.02–7.5 mg/l of As(III) is toxic for the growth of seed plants [1]. In the U.S., the Safe Drinking Water Act of 1974 set the maximum contamination level for arsenic at 0.05 mg/l [2]. The generator of the waste is obligated to determine if the waste is classified as hazardous or non-hazardous, and to follow the land disposal restrictions and schedules listed in Section 66900 of Article 11, Title 22, California Code of Regulations. Section 66699(b) states that a waste containing aresenic at a total concentration greater than or equal to 500 mg arsenic per kg of water, or at a soluble concentration greater than or equal to 5 mg arsenic per liter is hazardous. Recovery and recycling of arsenic are desirable since current disposal methods for arsenic materials are expensive and possibly environmentally hazardous. It should be noted that the generator may be held responsible for the land-disposed waste at all future times.

With the growing use of GaAs in the manufacturing of electronic devices a considerable effort is justified to recover the valuable gallium and to remove the toxic arsenic material from the waste streams. There are more than fifteen steps to process GaAs crystals, including crystal growth, ingot sawing, wafer dicing, etching, cleaning, etc. Most of these steps will generate a waste slurry or solution. For example, the ingot sawing creates about 50% of the total waste in the form of a slurry, which contains a large amount of GaAs [3]. Treating the waste slurry streams is a high priority in the semiconductor industry since the slurries contain toxic arsenic and valuable gallium (worth about $150/kg). Table 1 shows that lapping and polishing steps produce waste streams with significant levels of arsenic, as well as non-hazardous materials.

Only two studies have reported treatment recovery processes for GaAs semiconductor waste. One study describes a filtration process to treat all liquids entering the GaAs slurry recovery system [4]. The waste streams for ingot cropping and wafer

Table 1 Composition and Arsenic Content of Lapping and Polishing Slurries

Slurry	Components	Initial Arsenic mg/L	Final Arsenic mg/L	Percent Removal
Lapping	GaAs, FeO, Al_2O_3, H_2O, Glycerol	30,000	3.1	99.99%
Polishing	GaAs, SiO_2, NaClO, $NaOCO_3$, H_2O	>120	1.1	>99.1

slicing were mixed together in one recovery unit, and those of lapping and polishing in another. After recovering solid waste (containing GaAs), the effluent of these two units entered a waste water treatment system to be treated further. A filtration and ion sorption system for recovering GaAs from the semiconductor process has been reported by Damico and Smith [3]. Only saw and dicer wastes were recovered with a settler apparatus. A part of the waste-water effluent from these settlers is recycled back to the system for cleaning the pipeline. The rest of the effluent is pumped to a filter, and an ion sorption system reduces the dissolved arsenic from the slurry. The adsorbed arsenic, including the sorbent, is packaged for off-site disposal.

During lapping, wafers are wax mounted to the lapper using a hot plate. On a machine with a set rotational speed, the wafers are lapped with an abrasive solution, pressure-fed onto the lapping surface. The lapping solution is a slurry of aluminum oxide, glycerol and water. After lapping the wafers are dismounted on a hot plate, rinsed in a soap solution and wiped dry. The wafers are then mounted on a polishing machine,

and polished with a sodium bicarbonate, sodium hypochlorite, water, and colloidal silica slurry.

More than 95% of the arsenic waste produced exists in the particulate form [4]. Rather than attempt to separate the inert particles from nontoxic particles, the strategy we have developed is to dissolve the gallium arsenide, separate the inert particles, and then evaporate water to recover gallium and arsenic in solid forms. This novel approach is simple, inexpensive and effective.

METHODS AND MATERIALS

The following is a step-by-step treatment plan that we have developed for the lapping polishing slurries.

Lapping Slurry Treatment:

The lap waste is a wet sludge containing GaAs, glycerol, alumina, iron oxide, and water. The concentration of arsenic in the untreated sludge exceeds 30,000 ppm. The following discussion provides a detailed analysis of the lapping slurry treatment shown in Figure 1. References are made to the step numbers appearing next to the boxes of Figure 1.

STEP 1: Obtain used lapping slurry.

STEP 2: Separate the liquid part of the slurry from the sludge by pouring the liquid into a container. Pour the sludge into a second container. This step will separate most of the glycerol from the slurry.

STEP 3: Add water to the sludge in a ratio of 2 parts water to 1 part sludge and tumble for 30 minutes to dissolve and thus remove the remaining glycerol from the sludge.

STEP 4: Settle the mixture of 4 hours.

STEP 5: Decant the liquid containing fine particles, water and glycerol into the first container discussed in step 2.

STEP 6: Prepare a mixture of 1 part ammonia hydroxide (NH_4OH), 1 part hydrogen peroxide (H_2O_2), and 1 part water. Add this etching solution to the sludge in a ratio of 1 to 1 and tumble for 30 minutes. This process dissolves the gallium arsenide as gallium and arsenic trioxides.

STEP 7: Settle the mixture for 5 hours.

STEP 8: Decant the liquid into a third container. This liquid contains dissolved arsenic and is considered hazardous.

STEP 9: Add water to the sludge (ratio of 2 to 1) and tumble for 30 minutes to dissolve the remaining soluble arsenic. Repeat steps 7 through 9 three times.

STEP 10: Add 1 molar nitric acid (HNO_3) to the sludge (ratio of 2 to 1) and tumble for 30 minutes. This step further oxidizes arsenic trioxide to arsenic pentoxide and also dissolves the iron oxide.

STEP 11: Settle the mixture for 5 hours.

STEP 12: Decant the liquid into the third container discussed in step 8.

STEP 13: Add water to the sludge (ratio of 2 to 1) and tumble for 30 minutes to dissolve the soluble arsenic pentoxide.

STEP 14: Settle the mixture for 5 hours.

STEP 15: Decant the liquid into the third container discussed in step 8. Repeat steps 13 through 15 four times.

STEP 16: The solid obtained from step 15 is aluminum oxide. This mixture is considered non-hazardous and can be recycled as fresh lapping slurry by mixing with water and glycerol.
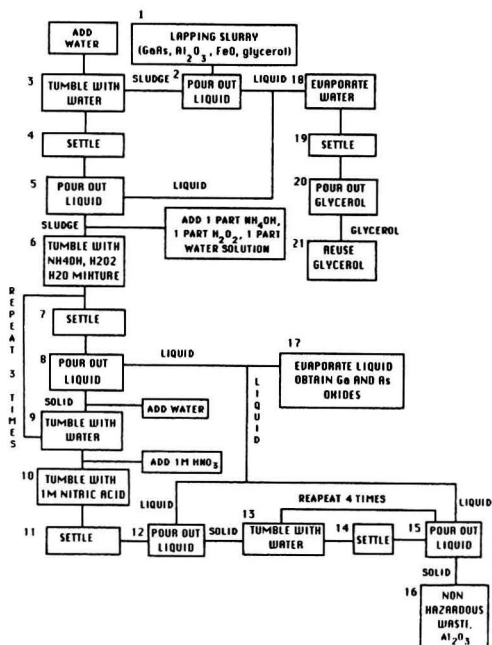

FIGURE 1. Lapping slurrgy treatment.

STEP 17: Evaporate the water from steps 8, 12, and 15 to obtain gallium and arsenic oxides, which are then recycled.
STEP 18: Evaporate the liquids from steps 2 and 5 to obtain glycerol mixed with some aluminum oxide particles (grit).
STEP 19: Settle the glycerol/grit mixture for 4 hours.
STEP 20: Decant the glycerol into a container.
STEP 21: Recycle (or dispose) the pure glycerol obtained from step 20.

Polishing Slurry Treatment:

The polishing slurry is a solution containing dissolved GaAs, colloidal silica, sodium bicarbonate, sodium hypochlorite, and water. The concentration of arsenic in the untreated solution exceeds 120 ppm. The following is a discussion of the polishing slurry treatment in Figure 2. References are made to the step numbers that appear next to the boxes in Figure 2.

STEP 1: Obtain polishing slurry.
STEP 2: Evaporate the water to obtain gallium and arsenic salts mixed with non-hazardous solids.
STEP 3: Add water in a ratio of 2 parts water to 1 part solid and tumble for 30 minutes. This will dissolve the gallium and arsenic salts.
STEP 4: Settle the mixture for 4 hours.
STEP 5: Decant the liquid into a second container. Treat the solid by following steps 3 through 5 six times.
STEP 6: Evaporate the liquid from step 5 to obtain pure gallium and arsenic salts.
STEP 7: The treated solid from step 5 is silica and is considered non-hazardous.

FIGURE 2. Polishing slurry treatment.

RESULTS AND DISCUSSION

The effectiveness of the arsenic removal from lapping and polishing slurry treatments in summarized in Table 1. The percent removal of arsenic for both lapping and polishing slurries is greater than 99%. Moreover, the treated lapping slurry was analyzed to have less than 0.16 ppm lead (Pb) and 0.49 ppm nickel (Ni), which is considerably less than the maximum amount of 0.4 ppm and 2.6 ppm, respectively, allowed by the EPA.

As stated previously section 66699(b) of Article 11, Title 22, California Code of Regulations, entitled "Criteria for Identification of Hazardous Wastes," shows that a waste that contains arsenic at a total concentration greater than or equal to 500 milligrams arsenic per kilogram of waste (mg/kg), or at a soluble concentration greater than or equal to 5 milligrams arsenic per liter is considered hazardous. The results of tests for arsenic in the treated lapping and polishing slurries in Table 1 correspond to the soluble arsenic as measured by the Waste Extraction Test in Section 66700, Title 22, by a commercial laboratory certified to perform hazardous waste analysis.

During the treatment of the sludge with the etching solution arsine gas is given off in an amount of much less than 0.05 ppm, as measured by an arsine gas detector. The maximum allowable concentration of arsine gas in the air is 0.05 ppm, according to the California Department of Health Services. The vapor from the evaporation process was also analyzed and found to contain less than the allowable 0.01 ppm arsenic when the vapor system is diluted with air.

The lapping waste contains a significant amount of glycerol, which reacts exothermically with the etching solution. A trial demonstrated that 100 ml of glycerol added to 1 L of etching solution caused an increase of 5°C. Therefore, to increase the effectiveness of the etching solution for oxidizing the arsenic, glycerol was removed from the sludge before the arsenic was reacted with the solution.

Another experiment addressed the possible reactions between 316 stainless steel and the etching solution. Stainless steel dissolves in the solution, limiting the usage of the steel containers for lapping and polishing treatment processes. Polyethylene containers are now resistant to the etching solution and are cost effective for these processes.

A cost evaluation of these recycling processes indicates that the apparatus needed will cost less than $10,000 to treat 3 and 7 barrels/year of lapping and polishing slurries, respectively. In addition to the initial capital investment, the cost of energy for evaporation of water is a substantial expense. A 20 kw heater will serve to evaporate 2.0 gal water/hr. At $0.10/kw.hr for the 20 kw evaporator operating 3000 hr/year, the energy cost is $6000/year. The current methods of disposing of these slurries result in payments for waste transport and for landfill usage. Moreover, the generators are held accountable for these wastes even after disposal. Treating the water on-site for recovery and recycle of gallium and arsenic, as described here, has distinct advantages over shipping and disposing the untreated hazardous waste off-site.
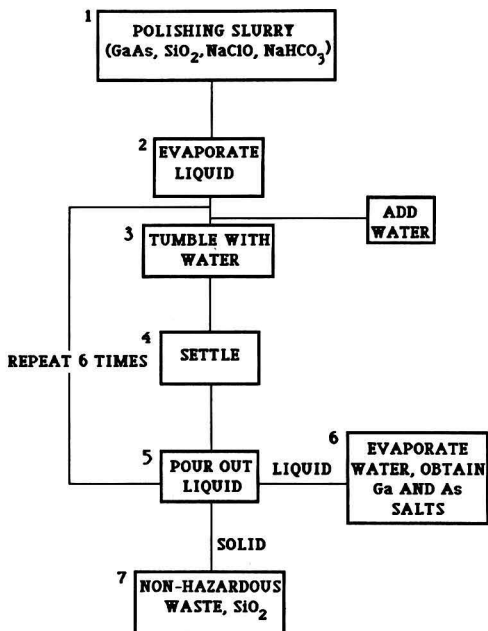
ACKNOWLEDGMENT

LITERATURE CITED

1. Bowen, H. J. M., *Environmental Chemistry of the Elements*, Academic Press, London (1979).
2. Ghosh, M. M., and R. S. Teoh, "Adsorption of Arsenic on Hydrous Aluminum Oxide," *Proceedings of the 17th Mid-Atlantic Industrial Waste Conference*, Ed. by I. J. Kugelman, 139 (1985).
3. Damico, F. A., and O. F. Smith, "Toxic and Recoverable Wastes from III-V Compound Semiconductor Manufacture," *Proceedings of the Mid-Atlantic Industrial Waste Conference*, 11, 157 (1979).
4. *Final Report to State of California, Department of Health Services*, Application to Study the Reduction of Arsenic Wastes in the Electronics Industry, Envirosphere Co./Hewlett-Packard Co., (June, 1987).

Preliminary Studies on the Granular Activated Carbon-Sequencing Batch Biofilm Reactor

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The Granular Activated Carbon-Sequencing Batch Biofilm Reactor (GAC-SBBR), a system which combines a submerged membrane oxygenation system to support a biofilm with granular activated carbon (GAC), and the Sequencing Batch Biofilm Reactor (SBBR), a comparable system containing no GAC, were investigated to determine the efficiency of each for the treatment of wastewaters containing volatile components. Toluene, at feed concentrations between 100 and 200 mg/L, was reduced to less than 10 µg/L in both systems. In the GAC-SBBR, biodegradation and adsorption were responsible for 92% and 8%, respectively, of the toluene removal, while in the SBBR, all of the toluene was removed by biodegradation. The quantity of toluene volatilized from the GAC-SBBR over a 10 week period of operation was approximately 0.003% of the toluene introduced. The major consideration for long-term, efficient operation of these systems is selection of an operating strategy which results in the supply of sufficient oxygen to the biomass. Both biomass wasting and purging of the membrane oxygenation system were critical for maintaining adequate oxygen transfer to the biofilm in the GAC-SBBR and in the SBBR.

INTRODUCTION

Sequencing Batch Reactor

The Sequencing Batch Reactor (SBR) has been used to treat both domestic and industrial wastewaters [1]. Because of the time-oriented nature of the SBR, simple operational modifications can alter the nature and extent of nutrient removal [2, 3, 4, 5, 6] and can be used to control bulking sludge, a common problem in continuous flow wastewater treatment systems [7].

Conventional Aeration Systems

SBRs in both research and in full-scale operation have been typically operated as suspended growth systems and have utilized mechanical and/or diffused aeration to provide oxygen to the biomass [1]. As a result of increasingly stringent requirements for minimization of air emissions, volatile organic compounds that are air stripped from these systems will need to be trapped and treated. Alternative aeration devices that reduce or even eliminate these emissions are desired.

Agitation associated with mechanical and diffused aeration equipment may also cause foaming in reactors containing agents that reduce surface tension. Such foaming can interfere with oxygen transfer and cause anoxic or anaerobic conditions in the reactor and other associated problems such as the production of nonbiodegradable intermediates, undesirable population shifts, and reactor failure [8, 9].

Membrane Oxygenation

In order to avoid some of the difficulties discussed above for conventional aeration systems, oxygen supply with gas-
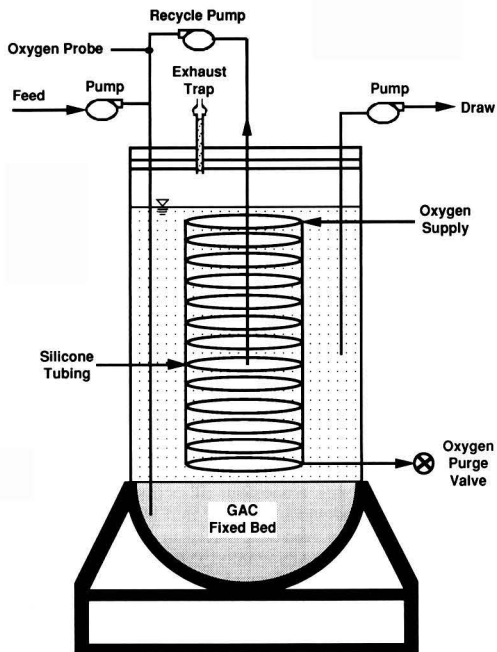
FIGURE 1. Bench-scale Granular Activated Carbon-Sequencing Batch Biofilm Reactor (GAC-SBBR)

permeable membranes has been investigated. One of the earliest applications of such a system utilized silicone rubber membranes for auxiliary oxygenation of an SBR designed to treat wash water from a honey processing plant [8]. In this particular system, peak oxygen demands in the SBR could not be met with diffused aeration alone. The resulting extended anoxic periods (i.e., beyond an intentional and desirable anoxic fill period) led to accumulation of fermentation products which lowered the pH in the reactor and caused high effluent organic concentrations. Increasing the rate of diffused aeration caused foaming of the reactor contents without overcoming the oxygen deficit.

In an attempt to provide additional oxygen to the reactor under less vigorous conditions (to prevent foaming), a coil of silicone tubing was installed in the reactor. Pure oxygen was passed through the lumen of the tubing during the aeration phase of each cycle. The additional oxygen provided via diffusion through the silicone tubing prevented extended anoxic periods and rapidly led to improved reactor performance.

In the previously described study, the author [8] expected that attachment and growth of biomass on the submerged coil of silicone tubing would occur and would hinder oxygen transfer through the tubing. Surprisingly, the investigators found that when the silicone tubing was loaded with pure oxygen, very little biofilm growth occurred. However, when the tubing was loaded with a diluted gas stream (e.g., air), biofilm growth was much more extensive and interfered significantly with the supply of oxygen to the reactor. It was assumed that the supply of pure oxygen to the silicone tubing led to toxic oxygen concentrations on the surface of the membrane.

Additional work by Wilderer [8, 9] on membrane systems for oxygenation of wastewater treatment systems also reported that silicone membranes loaded with pure oxygen would not support biofilm growth due to toxic oxygen concentrations at the surface. In a later study by Smith [10], however, it was found that silicone tubing loaded with pure oxygen supported biofilm attachment and growth that eventually interfered with oxygen transfer through the membrane.

Biofilm Reactors

In the studies discussed above, the reduced oxygen transfer caused by the biofilm growth on the submerged membrane was considered detrimental to the operation of the system. If designed for direct treatment instead of oxygen supply to a suspended growth system, the following operational and performance advantages can be realized if a balance between reduced oxygen transfer and biofilm growth can be achieved:
- enhanced biodegradation of low strength wastewaters
- maintenance of large numbers of slow-growing organisms
- maintenance of organisms with poor settling characteristics, which would wash out in suspended growth systems
- minimization of air stripping of volatile components in the wastewater by supplying oxygen to the biomass under relatively quiescent conditions.

Activated Carbon Enhancement

Treatment for wastewaters containing low concentrations of hazardous organics often involves adsorption on granular activated carbon (GAC) as a final step after biological treatment [11, 12]. Spent carbon is either disposed of or regenerated, typically using physical processes. Though seldom used in practice, biological regeneration of activated carbon is also an option.

Ying [13] found that the addition of powdered activated carbon (PAC) to an SBR resulted in an effluent with extremely low contaminant concentrations. The overall cost of this system, in terms of carbon usage, was found to be less than that for either a single stage system which used GAC alone or a two stage system which consisted of biological treatment in an SBR followed by carbon adsorption. In addition to bioregeneration of PAC in this system, PAC enhancement also serves to buffer peak loadings to the reactor as well as maintaining high effluent quality in the event of a reduction in biological activity or the introduction of non-biodegradable compounds to the reactor.

Granular Activated Carbon-Sequencing Batch Biofilm Reactor

A system combining a submerged membrane oxygenation system supporting a biofilm, and enhanced with GAC, would provide excellent treatment capabilities for high strength wastewaters containing volatile components. Such a system was investigated in the current study.

Bench-scale studies on the Granular Activated Carbon-Sequencing Batch Biofilm Reactor (GAC-SBBR) and the Sequencing Batch Biofilm Reactor (SBBR) are described herein. The studies were directed at the development of strategies for operating the system. A synthetic wastewater containing a single, biodegradable, volatile compound (toluene) was utilized.

Biodegradation of Toluene

While toluene is not readily degraded by all microorganisms, several bacterial species, including, *Pseudomonas putida mt-2* [14], *P. putida F1* [15], *P. aeruginosa* [16], *P. mendocina* [17], and *bacterium G4* [18], have been reported to have toluene-degrading ability. *P putida mt-2* contains a plasmid, designated TOL, which contains the genetic information necessary to produce the enzymes for the degradation of toluene and related compounds (e.g., benzene, ethylbenzene, and xylenes).

This particular organism degrades toluene by oxidizing the methyl group to form benzoic acid, oxidizing benzoic acid to form catechol, and utilizing a dioxygenase for ring cleavage. The 2-hydroxymuconic semialdehyde formed by this ring cleavage is directed to the TCA cycle, where it is completely oxidized to CO_2 and H_2O. The other organisms mentioned utilize various other pathways to degrade toluene.

Adsorption of Toluene

In the GAC-SBBR, toluene will be removed by both adsorption to GAC and biodegradation. In typical wastewater applications, contact times are long and influent contaminant concentrations are fairly constant, so that equilibrium expressions such as the Freundlich isotherm ($X/M = KC_e^{1/n}$) can adequately describe such systems. In the GAC-SBBR, however, kinetics, and not equilibrium, is the governing factor since the concentration of toluene to which the carbon bed is exposed varies throughout a given cycle because of biological degradation.

MATERIALS AND METHODS

Experimental Apparatus

The bench-scale GAC-SBBR shown in Figure 1 was constructed using a 4 L cylindrical glass kettle. 300 grams of Filtrasorb 300 GAC was rinsed thoroughly in Milli-Q water, dried overnight in a 103°C oven, and placed in the bottom of the reactor to serve as a fixed carbon bed.

After addition of the GAC to the reactor, the silicone membrane oxygenation system was installed. This system consisted of 25 feet of silicone tubing (0.125″ ID × 0.1875″ OD) wrapped in a double layer approximately 4 inches long around a cylindrical support structure. The ends of the silicone tubing were connected to glass tubes fused through the wall of the reactor, with the inlet tube connected to an oxygen tank with a two-stage pressure regulator, and the outlet tube connected to a solenoid valve which allowed the pressure in the silicone tubing to be either held constant or purged, as desired.

A pure culture of *P. putida mt-2* maintained on a streak plate was used to grow the initial inoculum for the GAC-SBBR. Two liters of sterile nutrient media, amended with 2 mM methylbenzoate as an inducer for the TOL plasmid, and inoculated with *P. Putida mt-2* were incubated at room temperature for approximately 48 hours. 100 mL of the culture was then added to the GAC-SBBR. Prior to inoculation, the GAC-SBBR was operated according to the strategy described below for 9 days, during which approximately 2000 mg of toluene were introduced to the reactor and adsorbed on the GAC. After inoculation, the feed to the reactor was not sterilized, and, in general, aseptic practices were not followed. The addition of toluene as the sole carbon and energy source provided sufficient selective pressure to maintain a culture with toluene-degrading ability.

Reactor Operating Strategies

The reactor was operated in a sequencing batch mode with a total cycle time of 12 hours. The high water level (HWL) in the reactor was 3 L and the low water level (LWL) was 2 L, and two cycles were completed each day, giving the reactor a 1.5 day hydraulic residence time (HRT). Since a 4 L kettle was used, there was approximately a 1 L headspace in the reactor. The reactor sealed except for a carbon trap which collected any toluene which volatilized into this space and was displaced from the system during the fill period.

Table 1 Synthetic Feed Composition

Compound	Concentration (mg/L)
KH_2PO_4	727.6
Na_2HPO_4	305.3
$MgSO_4$	36.1
$CaCl_2 \cdot 2H_2O$	4.0
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.04
$FeSO_4 \cdot 7H_2O$	2.0
$ZnSO_4 \cdot 7H_2O$	2.0
$MnSO_4 \cdot H_2O$	0.4
$CuSO_4 \cdot 5H_2O$	0.04
$Co(NO_3)_2 \cdot 6H_2O$	0.04
$Co(Cl)_2 \cdot 6H_2O$	0.033
$Na_2B_4O_7 \cdot 10H_2O$	0.04
EDTA	1.0
$(NH_4)_2SO_4$	185.0
C_7H_8 (Toluene)	100–200 (see text)

The cycle began with a one hour fill period, during which 1 L of synthetic feed was introduced into the reactor with a peristaltic pump. The feed was placed in a 2 L bottle and pumped through Tygon tubing into the recycle line, such that the feed entered the reactor through the carbon bed. The composition of the synthetic feed is given in Table 1. For the first 23 weeks of operation, the feed was mixed on a daily basis by placing 2 L of nutrient media into a flask and adding 0.5 mL of toluene to the flask. The flask was then sealed and mixed overnight. When the feed was prepared in this manner, the toluene concentration introduced to the reactor varied between 100 and 130 mg/L. For the remainder of the study, the feed was mixed in a 20 L bottle by adding excess toluene (approximately 20 mL) to the nutrient media and allowing the solution to mix continuously. The feed supplied to the reactor was taken from the bottom of the bottle so that no free toluene was introduced to the reactor. When the feed was prepared in this manner, the toluene concentration varied between 170 and 200 mg/L.

The one hour fill period was followed by a 10 hour react period and then a one hour draw period, during which 1 L of treated effluent was removed from the reactor. Treated effluent was removed from the reactor from approximately mid-depth, outside the silicone coil, using a peristaltic pump.

Mixing during the entire operating cycle of the reactor was provided by recycle. The contents of the reactor was pumped out from the center of the silicone coil, at approximately mid-depth, past a dissolved oxygen (D.O.) probe, and then back into the reactor. The recycled liquid was reintroduced to the reactor at the bottom of the GAC bed at a rate of approximately

Table 2 Basic System Operating Characteristics for GAC-SBBR and SBBR

Period	Time (hours)
FILL	1
REACT	10
SETTLE	0
DRAW	1
IDLE	0
CYCLE	12
Cycles/day	2
Reactor volume	4 L
HWL	3 L
LWL	2 L
HRT	1.5 days
Recycle rate	300 mL/min
Oxygenation	See Table 3

Table 3 Oxygenation System Status

GAC-SBBR

Operational period (weeks)	Oxygenation system status
1	5 psig initially, reduced to 3 psig gradually over 1 week period
2–3	2 psig for entire cycle
4	1 psig for entire cycle
5–6	10 psig for first 2 hours of cycle/ 1 psig for remainder of cycle
7–15	1 psig for entire cycle
16	10 psig for first 3 hours of cycle/ 1 psig for remainder of cycle initially; increased to 10 psig for entire cycle gradually over 1 week period
17–33	10 psig for entire cycle

SBBR

Operational period (weeks)	Oxygenation system status
1–14	1 psig for entire cycle
15	2 psig initially, increased to 5 psig gradually over 1 week period
16–20	5 psig for entire cycle

300 mL/min. This recycle rate maintained well-mixed conditions in the reactor without disturbing the fixed carbon bed. A strip chart recorder was connected to the probe and continuously recorded D.O. concentrations in the reactor. A summary of the basic system operating characteristics is provided in Table 2.

Oxygen was supplied to the reactor by maintaining pressure in the silicone tubing for the entire operating cycle. When the GAC-SBBR was initially started, the pressure in the silicone tubing was set at 5 psig (at the oxygen cylinder). Throughout the study, this value was altered in response to varying D.O. concentration profiles in the reactor. In addition, for part of the study, the pressure in the tubing was maintained at a high value (i.e., 10 psig) for a fraction of an operational cycle and reduced to a lower value (i.e., 1 psig) for the remainder of the cycle. This strategy was utilized to investigate oxygen supply during periods of high demand (i.e., during fill). The status of the oxygen supply system throughout the study is described in Table 3.

In previous studies on membrane oxygenation systems, oxygen (or air) was allowed to constantly flow through the silicone tubing, purging any by-products which diffused into the tubing. In the current study, the silicone tubing was pressurized with oxygen (not flowing) and purged for 30 seconds each hour by opening the solenoid valve and allowing the oxygen to flow through the tubing. During the seventh and eighth weeks of operation of the GAC-SBBR, experiments were performed to determine the effect of periodic purging on oxygen transfer into the reactor. The solenoid valve was left closed for three consecutive cycles during week seven and for four consecutive cycles during week eight. The reactor was operated normally (i.e., with purging) between these experiments.

During the entire study, only two major changes in the operation of the GAC-SBBR occurred. The first was a two day experiment during which the biofilm was removed from the reactor for approximately two days and then reinstalled. Some of the biomass sloughed off the silicone tubing during this time and was not returned to the reactor. In addition, some biomass which had sloughed off the silicone tubing prior to this experiment and had settled on top of the GAC bed was also removed. This occurred during the 23rd week of operation. The second was the change in feed composition described previously.

A second reactor, hereafter referred to as the Sequencing Batch Biofilm Reactor (SBBR), was assembled approximately 21 weeks after the GAC-SBBR. The SBBR was identical to the GAC-SBBR in design except that this reactor contained no GAC bed. Operation of the SBBR was also very similar to that of the GAC-SBBR, the only differences being the oxygen pressure in the tubing and the purge period, which was only 10 seconds each hour in the SBBR. The status of the oxygen pressure in the silicone tubing in the SBBR is detailed in Table 3. Approximately nine weeks after operation of the SBBR began, biomass was intentionally removed from the biofilm by washing the silicone coil with a steady stream of water, and the impact on oxygen transfer and toluene utilization determined. This experiment was repeated during the 18th week of operation.

Reactor Analyses

In addition to the D.O. concentration profiles, collected regularly on both the GAC-SBBR and the SBBR, liquid samples were periodically collected from both reactors during an entire operational cycle so that the accumulation and disappearance of toluene could be tracked. The samples were collected through the top of the reactors using glass pipettes, placed in 7.4 mL vials with teflon-lined caps, and acidified with two drops of concentrated hydrochloric acid. Samples not analyzed immediately were stored at 4°C. Samples were never stored for more than 7 days.
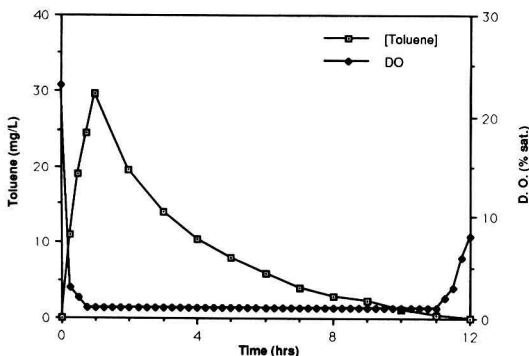

FIGURE 2. Toluene and D.O. concentration profiles with oxygen at 1 psig for GAC-SBBR
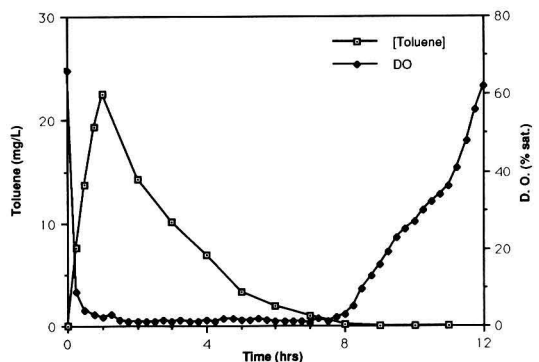

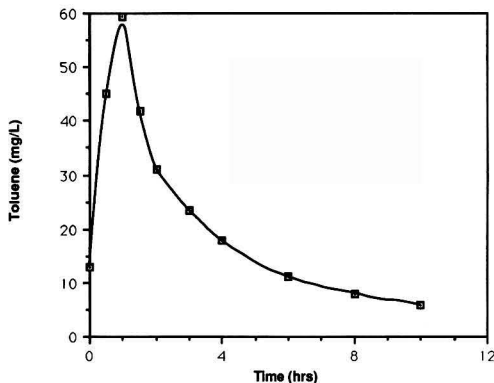**FIGURE 3. Toluene and D.O. concentration profiles with oxygen at 10 psig for GAC-SBBR**

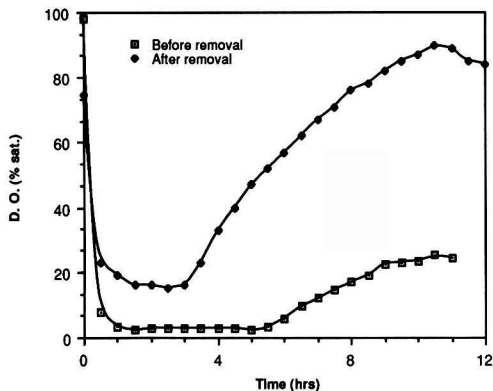**FIGURE 4. Toluene profile with oxygen at 10 psig at conclusion of study for GAC-SBBR**

FIGURE 6. Dissolved oxygen profiles before and after removal of biomass in the GAC-SBBR

Analysis of toluene in the liquid samples was performed using a Tekmar LSC-2 purge and trap concentrator and a Varian 3700 GC with PID detector according to method 6220 B in *Standard Methods* [19]. Extraction of reactor carbon traps and the GAC bed in the GAC-SBBR for toluene analysis was performed according to OSHA method #12 [20]. These samples were also analyzed on a Varian 3700, but were injected on-column and utilized an FID detector.

Suspended solids analysis of reactor effluent was initially performed according to method 2540 D in *Standard Methods* [19]. Since the microorganisms not associated with the biofilm did not flocculate well, much of the effluent turbidity passed through the standard glass fiber filters called for in this method. For this reason, 0.45 μm filters were used for the suspended solids analysis, thus providing a more accurate measure of the particulates present in the effluent.

All chemicals used in this experiment were ACS grade or better and are commercially available. The silicone tubing used in this experiment was obtained from Cole-Parmer (Chicago, IL.).

RESULTS

The results of two GAC-SBBR track studies in which the oxygen pressures in the silicone tubing were 1 psig and 10 psig

are presented in Figures 2 and 3, respectively. The corresponding D.O. concentration profiles are also shown. The influent concentrations of toluene were 128 mg/L for Figure 2 and 101 mg/L for Figure 3. Both of these studies were conducted after the GAC-SBBR had been operated for long periods of time (i.e., after 15 weeks for Figure 2 and 17 weeks for Figure 3) with no intentional biomass removal from the biofilm. Track studies were not performed on the GAC-SBBR earlier in the study.

The results of a track study performed just before the GAC-SBBR was shut down is shown in Figure 4. The oxygen pressure in the tubing was at 10 psig and the influent toluene concentration was 181 mg/L. The D.O. concentration in the reactor was zero throughout the entire cycle.

D.O. concentration profiles in the GAC-SBBR obtained during the first set of silicone tubing purge experiments are presented in Figure 5. Cycles one through three are three consecutive cycles during which the silicone tubing was not purged, while cycles four and five represent the next two cycles after the reactor was returned to its normal operating strategy (i.e., a 30 second purge of the tubing each hour).

D.O. traces obtained before and after the removal of excess biomass from the GAC-SBBR are shown in Figure 6, and clearly show that excess biomass has marked effects on D.O. concentrations in the reactor. A toluene track study was not performed after biomass removal in the GAC-SBBR. The results of toluene track studies before and after biomass removal
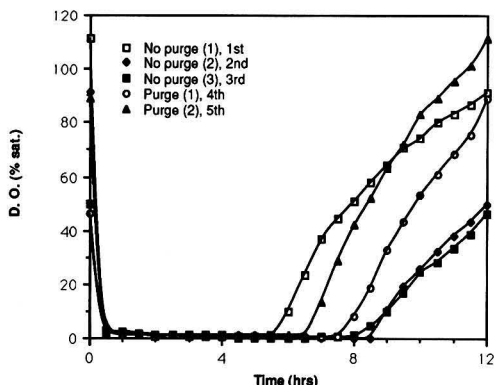

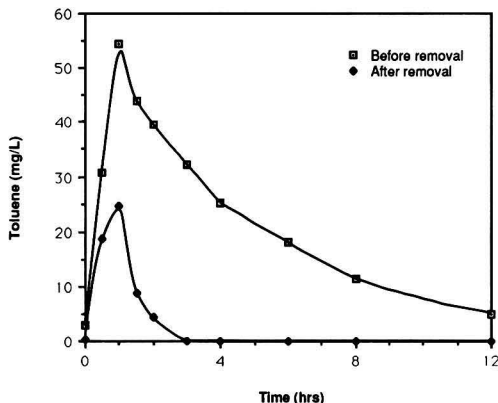**FIGURE 5. Dissolved oxygen profiles during purge test for GAC-SBBR**

FIGURE 7. Toluene concentration profiles before and after removal of biomass in the SBBR

in the SBBR during week 18, however, are shown in Figure 7. The concentration of toluene in the feed during this study was 198 mg/L for the cycle before biomass removal and 194 mg/L for the cycle after biomass removal.

After 33 weeks of operation, the GAC-SBBR was shut down and the carbon bed was thoroughly mixed and extracted to determine the quantity of toluene adsorbed. Duplicate samples yielded a toluene concentration of 23 mg/g of activated carbon in the reactor. This represents a total mass of toluene of 6900 mg, or approximately 8% of the total mass of toluene fed to the reactor, including the 2000 mg supplied before the reactor was inoculated.

The carbon trap which collected toluene which volatilized from the GAC-SBBR was removed after approximately 16 weeks of operation and was found to contain toluene concentrations below the detection limit of the analytical procedure. A smaller trap utilized for the next 10 weeks of operation contained approximately 0.5 mg of toluene, which is about 0.003% of the total mass introduced to the reactor during this period. The trap used for the remainder of the study was not analyzed.

The concentration of effluent suspended solids were determined for the GAC-SBBR to estimate the relative fraction of biomass preferentially attaching to the silicone tubing to that existing in suspension. Since there was no settle period in the operational cycle, the effluent and reactor suspended solids concentration were identical. The effluent suspended solids concentration varied between 20 and 36 mg/L for the first six weeks after startup. Thereafter, the value was typically below 10 mg/L until approximately 28 weeks into the experiment. At this time, other measurements (i.e., D.O. profiles and effluent toluene concentrations) suggested a decline in the performance of the GAC-SBBR and the effluent also started to become more turbid. No suspended solids measurements were made during this time.

DISCUSSION

Reactor Track Studies

As can be seen from Figures 2 and 3, toluene accumulates in the GAC-SBBR during the fill period and then is rapidly removed during react until the concentration is reduced to a very low level (typically less than 10 μg/L). Removal of toluene also took place during fill. The concentration of toluene after fill would have been 43 mg/L and 34 mg/L instead of 30 mg/L and 23 mg/L (see Figures 2 and 3), respectively, if no adsorption or biological degradation had taken place.

Typical D.O. concentration profiles show that the D.O. starts at an elevated level (e.g., 65% of saturation in Figure 3) and rapidly drops to a low level shortly after the beginning of the fill period. The D.O. remains low until the toluene concentration reaches about 1 mg/L, and then begins to increase until the next fill period begins. The shape of the D.O. profiles was fairly reproducible from cycle to cycle, while the actual D.O. values at the beginning and end of each cycle varied with the concentration of toluene in the feed and the oxygen pressure in the silicone tubing. Higher levels of toluene in the feed and/or lower oxygen pressure in the tubing delayed the time at which the D.O. began to increase. These conditions resulted in lower D.O. levels at the end of the cycle, and, consequently, at the beginning of the next cycle. Lower levels of toluene in the feed and/or increased oxygen pressure in the tubing caused higher D.O. levels at cycle end. Whenever the D.O. increased from zero during the later stages of the react period, the toluene concentration was ultimately reduced to low μg/L levels in the cycle time provided. For a given oxygen pressure in the tubing, however, the cycle time became less and less adequate as the total number of cycles increased. In

the final analysis, a steady decline in reactor performance could only be corrected by wasting biomass from the biofilm.

The data presented in Figures 2 and 3 were collected after the GAC-SBBR had been operated for an extended period of time and large quantities of biomass had accumulated in the reactor. During the early stages of GAC-SBBR operation, very little biomass had accumulated in the reactor and the D.O. concentration of the liquid in the reactor was typically above air saturation at the start of a cycle, dropped slightly during the fill period, and then quickly climbed back to supersaturated levels. Although no toluene track studies were performed early in the operation of the GAC-SBBR, such studies were done on the SBBR. Several days after inoculation, a track study on the SBBR, with the oxygen pressure at 1 psig, revealed toluene concentration profiles very similar to those presented in Figures 2 and 3. A large fraction of the toluene was removed during fill and the toluene concentration was reduced to low μg/L levels during the subsequent react period. The D.O. profiles in the SBBR during this time were similar to those described above for early operation in the GAC-SBBR.

After biomass was removed from the GAC-SBBR during week 23, the biomass was allowed to accumulate in the reactor to such an extent that the D.O. concentration remained at zero for the entire cycle. As shown in Figure 4, toluene accumulation during fill was to levels that can be accounted for by dilution alone when the D.O. remained at zero for the entire cycle. During the subsequent react period, the toluene was slowly removed, such that the effluent at the end of the cycle was about 5 mg/L.

Operation of the GAC-SBBR was discontinued at this time. Clearly, however, removing excess biomass from the reactor, or increasing the cycle time to allow for reactor recovery would have enabled continued operation of this reactor.

Oxygen Transfer Studies

A two-pressure oxygenation system was used to supply more oxygen to the reactor during periods of higher demand (i.e., during fill) and less when the toluene had been reduced to lower concentrations and the oxygen demand had decreased. This system delayed the onset of the near-zero D.O. conditions seen in Figures 2 and 3, but otherwise had little effect on the D.O. profiles and was removed shortly after being installed. When the oxygen demand in the GAC-SBBR could no longer be met with the oxygen pressure at 1 psig (as a result of accumulated biomass), the two-pressure oxygenation system was reinstalled, but was also unable to meet the increased demand. The pressure was increased to 10 psig for the entire operational cycle and maintained at this level for the remainder of the study.

As can be seen from Figure 5, the first set of silicone tubing purge experiments in the GAC-SBBR clearly demonstrate that the purge is necessary to maintain adequate oxygen transfer to the reactor. Elimination of the purge delays the time into the cycle at which the D.O. increased above zero and reduces the maximum D.O. concentration in the reactor. Both of these conditions reversed after purging. Results obtained from the second set of purge experiments were essentially the same as those obtained from the first. During the second set of experiments, however, a fourth no-purge cycle was accompanied by zero D.O. in the reactor for the entire cycle.

Throughout both sets of purge experiments, both the concentration of toluene in the feed and the oxygen pressure in the tubing were essentially constant. In addition, the change in reactor biomass content over the time for each study (i.e., 2.5 and 3 days, respectively) was minimal. These studies provide clear evidence that the oxygen transfer rate into the reactor is adversely affected by the no-purge strategy. While the need for purging has not yet been determined, accumulation of toluene, CO_2, and/or other byproducts could reduce the partial pressure of oxygen in the silicone tubing, and cause the reduced

oxygen transfer rates observed. Mass transfer limitations through an increased boundary layer could also result in the same response.

Biomass Wasting

The accumulation of large quantities of biomass in the reactor, both in the form of a thick biofilm on the silicone tubing, and as large flocs of biomass which sloughed off the tubing and settled to the bottom of the reactor, is one of the factors responsible for the loss of efficiency in the GAC-SBBR. This is shown clearly in Figure 6, where the D.O. concentration profile is markedly improved by the removal of some of the biomass from the GAC-SBBR. Toluene concentration profiles for both before and after biomass removal in the SBBR during week 18 are shown in Figure 7. These results clearly demonstrate that the increased oxygen demand exerted by accumulated biomass reduces reactor efficiency and that reactor performance can be improved by removal of excess biomass. The toluene concentration profiles before and after biomass wasting during week nine (not presented) were similar to those obtained during week 18, but the improvement in performance was less dramatic because less biomass had accumulated during the first nine weeks of operation.

Carbon Adsorption

The GAC bed removed from the GAC-SBBR was found to contain approximately 23 mg of toluene per gram of activated carbon. Based on the Freundlich isotherm values for toluene on Filtrasorb 300 (K = 24.1 and 1/n = 0.44) [21], the concentration of toluene in the liquid phase in equilibrium with this carbon should have been approximately 1 mg/L. Clearly, the effluent concentration of 5 mg/L shown in Figure 4 is not in equilibrium with the carbon. Since this figure represents a situation equivalent to a partial failure of the biological activity in the GAC-SBBR (due to an inability to meet oxygen demand), it was expected that the GAC would adsorb the toluene to its equilibrium concentration (i.e., approximately 1 mg/L) if sufficient time and adequate mixing had been provided. The lack of mixing in the GAC bed and the short contact time in the reactor both contribute to the inability of the bulk liquid to reach equilibrium with the GAC.

The quantity of toluene recovered from the traps on the GAC-SBBR suggests that loss of toluene by volatilization from the GAC-SBBR is negligible. The GAC-SBBR can clearly be used to treat wastewaters that contain volatile components. Similar results were found for the SBBR.

A closer look at Figures 4 and 7 (before biomass removal) supports the general finding that the GAC-SBBR and the SBBR had very similar performance characteristics in terms of toluene removal, even though the SBBR contained no GAC. The higher rate of toluene removal shown in Figure 4 for the GAC-SBBR is likely the result of the higher oxygen pressure in the silicone tubing (i.e., 10 psig vs. 5 psig in the SBBR) and different biomass thicknesses. This similarity in performance is not surprising. The quantity of toluene adsorbed to the GAC in the GAC-SBBR was only about 8% of the total supplied to the reactor, and toluene is readily degraded by the microorganisms introduced into both reactors.

Based on the results reported in this preliminary investigation, there appears to be no significant difference between the SBBR and the GAC-SBBR, primarily because toluene is readily biodegradable at all soluble concentrations tested. The distinction between the SBBR and the GAC-SBBR becomes important when toxic compounds which are either toxic at high concentrations or are non-biodegradable are introduced to the reactors. In the GAC-SBBR, the quantity of GAC added to the reactor system can be adjusted so that toxic compounds

will adsorb to the GAC and remain below toxic levels. As the biological destruction of these toxic compounds takes place in the biofilm, their concentration in the bulk liquid phase will decrease and they will slowly desorb, thus regenerating the GAC. When such compounds are introduced to an SBBR with an inappropriate operating strategy (e.g., one with a fast fill), however, these compounds will likely accumulate to toxic concentrations before adequate biodegradation can take place. The ability of GAC to maintain low concentrations of toxic compounds in a sequencing batch biofilm reactor like system has been demonstrated by Jaar [22].

When toxic, non-biodegradable compounds are introduced to the GAC-SBBR along with biodegradable materials, adsorption will provide a non-toxic environment for the biofilm community to operate until the GAC requires thermal or chemical regeneration. In the SBBR, on the other hand, non-biodegradable compounds will quickly accumulate to toxic levels and thus reduce the overall rate of destruction of biodegradable compounds.

CONCLUSIONS

The results presented above demonstrate that both the GAC-SBBR and the SBBR are effective systems for long-term treatment of wastewaters containing volatile, biodegradable compounds, without concern for fugitive emissions. The major consideration for long-term operation of either of these systems is selection of an appropriate operating strategy to maintain sufficient oxygen supply to the biomass. Three important factors in the selection of such a strategy have been identified in the current research: 1) wasting of biomass, 2) purging of the silicone tubing, and 3) appropriate selection of cycle times. Although increasing the oxygen pressure in the silicone tubing will increase oxygen transfer to the reactor and improve operation for a short period of time, this strategy will not allow for prolonged efficient operation of either the GAC-SBBR or the SBBR. Studies directed at determining a more in-depth understanding of both biofilm wasting and tube purging are currently underway.

Further research into the kinetics of adsorption and the development of adequate mixing strategies must be investigated for wastewaters containing nonbiodegradable components. These factors must also be considered if the full potential for bioregeneration of GAC is to be realized.

Pilot-scale studies on the GAC-SBBR have been conducted and a full-scale GAC-SBBR is currently being designed for a toluene contaminated groundwater in the Southeastern U.S.A. At the present time, there are no known suppliers of the membrane aeration system.

LITERATURE CITED

1. Irvine, R. L., and L. H. Ketchum, Jr., "Sequencing batch reactor for biological wastewater treatment," *CRC Crit. Rev. Environ. Control*, **18**, 255 (1988).
2. Alleman, J. E., and R. L. Irvine, "Nitrification in the Sequencing Batch Reactor," *J. Water Pollut. Control Fed.*, **52**, 2747 (1980).
3. Palis, J. C., and R. L. Irvine, "Nitrogen Removal in a Low-Loaded Single Tank Sequencing Batch Reactor," *J. Water Pollut. Control Fed.*, **57**, 82 (1985).
4. Alleman, J. E., and R. L. Irvine, "Storage-Induced Denitrification Using Sequencing Batch Reactor Operation," *Water Res.*, **14**, 1483 (1980).
5. Manning, J. F., Jr., and R. L. Irvine, "The Biological Removal of Phosphorus in a Sequencing Batch Reactor," *J. Water Pollut. Control Fed.*, **57**, 87 (1985).

6. Ketchum, L. H., Jr., R. L. Irvine, R. E. Breyfogle, and J. F. Manning, Jr., "A Comparison of Biological and Chemical Phosphorus Removals in Continuous and Sequencing Batch Reactor," *J. Water Pollut. Control Fed.*, **59**, 13 (1987).

7. Chiesa, S. C., and R. L. Irvine, "Growth and Control of Filamentous Microbes in Activated Sludge: an Integrated Hypothesis," *Water Res.*, **19**, 471 (1985).

8. Wilderer, P. A., J. Brautigam, and I. Sekoulov, "Application of Gas Permeable Membranes for Auxiliary Oxygenation of Sequencing Batch Reactors," *Conservation & Recycling*, **8**, 181 (1985).

9. Wilderer, P. A., and I. Sekoulov, "Method to Biologically Treat Contaminated Soil Bodies," (unpublished).

10. Smith, G., "Treatability of Leachate from the Georgswerder Landfill Using Sequencing Batch Reactors with Silicone Membrane Oxygenation," (unpublished).

11. Irvine, R. L., S. A. Sojka, and J. F. Colaruotolo, "Enhanced Biological Treatment of Leachates for Industrial Landfills," *Haz. Waste*, **1**, 123 (1984).

12. Herzbrun, P. A., R. L. Irvine, and K. C. Malinowski, "Biological Treatment of Hazardous Wastes in the SBR," *J. Water Pollut. Control Fed.*, **57**, 1163 (1985).

13. Ying, W., R. R. Bonk, and S. A. Sojka, "Treatment of a Landfill Leachate in Powdered Activated Carbon Enhanced Sequencing Batch Bioreactors," *Environmental Progress*, **6**, 1 (1987).

14. Worsey, M. J., and P. A. Williams, "Metabolism of Toluene and Xylenes by Pseudomonas Putida (Arvilla) MT-2: Evidence of a New Function of the Tol Plasmid," *J. Bacteriology*, **124**, 7 (1975).

15. Finette, B. A., V. Subramanian, and D. T. Gibson, "Isolation and Characterization of *Pseudomonas Putida PpF1* Mutants Defective in the Toluene Dioxygenase Enzyme System," *J. Bacteriol.* **160**, 1003 (1984).

16. Kitagawa, M., "Studies of the Oxidation Mechanism of Methyl Group," *J. Biochem.*, **43**, 553 (1956).

17. Gibson, D. T., "Microbiol Metabolism of Aromatic Hydrocarbons and the Carbon Cycle," in: *Microbial Metabolism and the Carbon Cycle* (ed. by Hagedorn, S. R., R. S. Hanson, and D. A. Kunz) Harwood Academic Publishers, Chur, Switzerland, pp. 43–52 (1988).

18. Shields, M. S., S. O. Montgomery, P. J. Chapman, S. M. Cuskey, and P. H. Pritchard, "Novel Pathway of Toluene Catabolism in the Trichloroethylene-Degrading Bacterium G4," *Appl. Environ. Microbiol.*, **55**, 1624 (1989).

19. Clesceri, L. S., A. E. Greenberg, and R. R. Trussell (eds.), *Standard Methods for the Examination of Water and Wastewater*, 17th Ed., Amer. Pub. Health Assn., Washington D.C. (1989).

20. "OSHA Method #12: Benzene Analysis for Air and Bulk Samples," in: *Organic Methods*, OSHA Analytical Laboratory, Salt Lake City, Utah (1980).

21. "Carbon Adsorption Isotherms for Toxic Organics," *EPA Report*, EPA-600/8-80-023, Municipal Environmental Research Laboratory, Cincinnati, Ohio (1980).

22. Jaar, M. A. A., and P. A. Wilderer, "Granular Activated Carbon Sequencing Batch Biofilm Reactor to Treat Problematic Wastewaters," unpublished report, Technical University of Hamburg-Harburg, Germany.

Estimation of VOC Emissions Using the BASTE Model

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Emissions of volatile organic compounds (VOCs) from wastewater raises concerns as many VOCs are photochemically reactive and contribute to the formation of tropospheric ozone, and may be toxic with subsequent adverse affects on human health. Many municipal wastewater treatment facilities (WWTFs) and industries are, or will be, required to complete extensive VOC emissions inventories. Accurate VOC emission models are desirable to facilitate such inventories, and to serve as alternatives to resource-intensive air sampling at all processes within WWTFs. A flexible VOC fate model (Bay Area Sewage Toxics Emissions: BASTE) has been developed to simulate a wide range of treatment configurations within WWTFs. In addition to its ability to simulate complex treatment trains, BASTE has several features not found in existing VOC fate models. These features include the ability to 1) simulate covered treatment processes, 2) mix mechanistic emissions estimates with emissions measurements and empirical emission factors, and 3) incorporate measured dissolved oxygen concentrations as surrogate measures of VOC emission potential.

INTRODUCTION

Volatile organic compounds (VOCs) occur in both municipal and industrial wastewaters and cause several concerns including 1) emissions of toxic VOCs and subsequent health risks to treatment plant workers and the general public, and 2) emissions of reactive VOCs that contribute to the formation of ozone in urban air basins. These concerns have led to recent state and federal requirements to inventory VOC emissions at both industrial and municipal wastewater treatment facilities (WWTF). Emissions inventories will likely lead to requirements for controlling VOC emissions from many WWTFs.

To reduce the costs and complexities associated with direct air sampling at all wastewater treatment processes, several emissions estimation methods have been developed based on analysis of aqueous samples. The conservative mass loading (CML) method utilizes wastewater flow rates coupled with VOC influent concentrations to calculate VOC influent mass loadings. The influent mass loadings are assumed to equal VOC emissions from an entire WWTF. This method requires liquid sampling at only one location. However, it is conservative as it does not account for biodegradation, sorption, and plant pass through. It can also underestimate emissions of chloroform which forms following pre and post-chlorination. The CML may still provide a reasonable approximation of emissions for highly volatile, recalcitrant VOCs, and can be used as a relatively inexpensive screening method to justify the need, or lack thereof, of additional studies.

The conservative mass balance (CMB) method is based on the difference in VOC mass loadings in WWTF influent and effluent streams. Overall mass removals from a facility are attributed entirely to volatile emissions. This method requires liquid sampling at two locations, with the added complexity of accounting for hydraulic residence time through a WWTF.

Like the CML, the CMB is conservative for most VOCs as it does not account for biodegradation and sorption losses. However, it may still be a useful screening method to determine whether further emissions studies are necessary.

The CML and CMB emissions estimates can be multiplied by an emission factor which accounts for the fraction of mass loading or loss attributed to volatile emissions. This reduces the conservative nature of both the CML and CMB. However, stripping factors are not readily available for many VOC/process combinations, and those that are do not account for plant characteristics that enhance or retard emissions.

The emissions estimation methods described above pose the problem of not indicating the primary sources of VOC emissions within WWTFs. Such information is useful for the design of VOC control systems and assessment of simple process modifications to reduce emissions. Furthermore, process-specific emissions estimates may be required for transport models used in risk assessments. The CMB can be used to estimate volatile losses from individual processes. However, VOC concentration reductions across many processes are generally of the same order as, or smaller than, uncertainties in sampling and analysis methods. This leads to high uncertainties in process-specific emissions estimates.

As an alternative to the emissions estimation methods described above, general fate models (GFMs) have been developed to simulate competing removal mechanisms (volatilization, biodegradation, sorption) for VOCs in wastewater. Model input requirements for GFMs usually include concentrations of VOCs in plant or process influent, VOC properties, wastewater flow rate, and process-specific operating parameters, although input requirements and degree of modeling detail varies significantly between GFMs. For most GFMs, output is in the form of multi-mechanism mass flows at individual processes. However, many GFMs are restricted to activated sludge reactors and associated clarifiers. Thus, they do not attempt to simulate the fate of VOCs in aerated channels and grit chambers, trickling filters, weirs, and other processes preceding or proceeding activated sludge treatment.

This paper provides a description of a new GFM that is generally more flexible than existing GFMs in its ability to simulate a wide range of treatment configurations. It is intended to serve initially as a screening model, but has been structured to evolve into a detailed simulation tool as field data become available for model evaluation.

BACKGROUND

Several models have been developed to simulate the fate of VOCs in wastewater (Barton [2], Blackburn [3], Govind et al. [8], Namkung and Rittmann [12]). Most of the existing models are based on an assumption of steady-state conditions, and are similar in terms of mathematical expressions used to simulate the fate of VOCs. Major differences between individual models include 1) application of different methods to calculate variables required in fate expressions, e.g. biological rate constants and mass transfer coefficients, 2) number and type of treatment processes that can be simulated, 3) number and types of compounds for which the model is applicable, 4) mass transfer assumptions, e.g., saturated versus unsaturated air bubbles, and 5) model flexibility in terms of ability to simulate a wide range of treatment configurations and process-specific operating conditions.

Mechanisms which are believed to most influence the fate of VOCs during wastewater treatment are 1) sorption to solid particles and biomass, 2) biodegradation, and 3) volatilization. A brief description of each mechanism is provided below.

Adsorption to Solid Particles and Biomass

Volatile organic compounds adsorb to solid particles during transport in wastewater collection systems, with subsequent removal in primary sludge streams. Furthermore, VOCs can adsorb to biomass during biological treatment, with subsequent biodegradation or removal in waste activated sludge streams. While there has not been a great deal of published literature regarding adsorption of VOCs to solids in wastewater, it is generally agreed upon that adsorption losses for VOCs are small relative to those caused by volatilization and biodegradation (Petrasek et al. [16], Chang et al. [4]). Furthermore, the sorption process for many organic contaminants is partially and often fully-reversible (Tsezos and Bell [20]). It has also been shown that adsorption of VOCs is enhanced by an increase in organic carbon content of particles (Dobbs et al. [6], Karickhoff et al. [9]).

Adsorption of VOCs at low concentrations and equilibrium can be modeled by linear isotherms of the form

$$q = K_p C_l, \tag{1}$$

where q is the mass of contaminant sorbed to solids per mass of solids (mg/mg), C_l is the contaminant concentration in wastewater (mg/m^3), and K_p is the liquid-solid partition coefficient (m^3/mg-solids). Once q has been estimated, the rate of VOC removal to sludge streams, R_s, can be calculated as

$$R_s = -Q_w X q, \tag{2}$$

where R_s has units of mg/s, Q_w is wasted sludge flow rate (m^3/s), and X is the concentration of solid particles or biomass (mg/m^3).

The octanol/water partition coefficient (K_{ow}) for a specific compound is defined as the ratio of contaminant concentration in n-octanol to its concentration in water at equilibrium. A high K_{ow} implies that a contaminant has a high affinity for adsorbing to organic phases in solution, including organic particles and biological solids. Thus, empirical models to estimate K_p have relied on correlations of experimental data with K_{ow}.

Karickhoff et al. [9] studied adsorption of 10 hydrophobic compounds to pond and river sediments. The value of K_p was observed to be related to organic carbon content of solids, and the following empirical relationships were developed:

$$K_p = g K_p', \tag{3a}$$

$$K_p' = 6.3 \times 10^{-7} K_{ow}, \tag{3b}$$

where g is the fraction of mass of organic carbon in solids (g/g), K_p' has units of m^3/g-TSS (TSS = total suspended solids), and K_p has units of m^3/g-VSS (VSS = volatile suspended solids). Namkung and Rittmann [12] used Equations (3a) and (b) to estimate adsorption of VOCs to biomass and represented a biological cell of the structure $C_5H_7O_2N$. Thus, $g = 0.531$ and Equations (3a) and (3b) for biological reactors were rewritten as

$$K_p = 3.345 \times 10^{-7} K_{ow}. \tag{4}$$

Dobbs et al. [6] developed a relationship for K_p based on K_{ow} and modified Randic indexes for 6 VOCs (methylene chloride, chloroform, 1,1-dichloroethene, carbon tetrachloride, chlorobenzene, and tetrachloroethene) and 6 semi- and non-volatile organic compounds. The fraction of organic contaminants sorbed to solids was accounted for by Equation (3a) and the relationship

$$\log_{10}(K_p') = 0.58 \log_{10}(K_{ow}) + 1.14, \tag{6}$$

where K_p' has units of liters/kg. Equations (3a) and (6) were observed to be consistent for adsorption to primary solids, mixed liquor solids, and digested solids as long as the organic content of the solids was considered.

Biological Degradation

Biodegradation losses can be estimated using the Monod kinetics model

$$R_b = \frac{-kX_aC_lV}{K_s + C_l},$$ (7)

where R_b is the mass rate of biodegradation (mg/s), k is maximum specific substrate utilization (mg/mg-VSS·s), X_a is active cell concentration (mg-VSS/m^3), K_s is the Monod half-velocity constant (mg/m^3), C_l is compound concentration in the aqueous phase (mg/m^3), and V is reactor volume (m^3). At low VOC concentrations, typical of most municipal wastewaters, $K_s \gg C_l$ and Equation (7) can be approximated by

$$R_b \approx \frac{-k}{K_s} X_aC_lV = k_1X_aC_lV,$$ (8)

where k_1 is an effective first-order (in C_l) biological rate constant for a specific VOC (m^3/mg-VSS·s).

A wealth of biodegradable compounds, i.e. as expressed as BOD, are available to serve as primary substrate in biological treatment processes. Because VOC concentrations are generally much lower than aggregate concentrations of biodegradable organic compounds, secondary utilization of VOCs is the likely biodegradation mechanism (Namkung and Rittmann [12]). However, despite this understanding, values of k_1 are not readily available for many VOCs. Namkung and Rittmann [12] suggested that typical values of k_1 range from 0.1 to 100 m^3/g-VSS·d, with very degradable compounds having k_1 in excess of 10 m^3/g-VSS·d. They noted that compounds which are difficult to degrade are likely to have k_1 less than 0.1 m^3/g-VSS·d. Furthermore, a GFM developed for a well-mixed activated sludge system was coupled with data obtained by Weber and Jones [22] for laboratory-scale reactors to back-calculate k_1 values for four VOCs. The values for chlorobenzene, ethylbenzene, benzene, and toluene were 0.21, 0.23, 0.32, and 0.40 m^3/g-VSS·d, respectively. These rate constants led to GFM predictions of greater than 94% biodegradation of each VOC in municipal activated sludge systems in Chicago (Namkung and Rittmann [12]).

Volatilization

Volatilization is defined here as the transfer of VOCs across a gas/liquid interface. It refers to stripping losses to submerged air bubbles, transfer from dispersed liquid particles to surrounding air, e.g. with surface aeration or splashing at the bottom of drop structures, and transfer across open wastewater surfaces, e.g. quiescent portions of clarifier or pond surfaces. For each type of volatilization mechanism, the rate of mass transfer can be defined as

$$R_v = -K_l\left(C_l - \frac{C_g}{H_c}\right)A,$$ (9)

where R_v is the rate of mass transfer (mg/s), K_l is an overall mass transfer coefficient for a specific compound (m/s), C_l is the aqueous VOC concentration (mg/m^3), C_g is the gaseous VOC concentration above a wastewater surface (mg/m^3), H_c is a dimensionless Henry's law constant defined as the ratio of gaseous to aqueous concentrations at thermodynamic equilibrium, and A is interfacial transfer area (m^2). The term C_g/H_c represents what the liquid concentration would be if it existed in thermodynamic equilibrium with a gas concentration of magnitude C_g.

According to two-film theory, K_l consists of both liquid and gas phase transfer resistances. However, for highly volatile compounds, gas phase resistance can be assumed to be negligible and Equation (9) is approximated by

$$R_v = -k_l\left(C_l - \frac{C_g}{H_c}\right)A,$$ (10)

where k_l is a liquid phase transfer coefficient (m/s).

The ratio of k_l values for volatile compounds has been shown to be insensitive to liquid temperature and degree of turbulent mixing (Tsivoglou et al. [21], Matter-Muller et al. [10], Smith et al. [19]). Because oxygen transfer coefficients are often known or can be readily estimated for many wastewater treatment processes, oxygen can be used as a volatile reference compound to estimate k_l values for VOCs. The following linear relationship results:

$$k_{1,voc} = \psi k_{1,O_2},$$ (11)

where $k_{l,voc}$ and k_{l,O_2} are liquid transfer coefficients for a VOC and oxygen, respectively, and ψ is referred to as a transfer coefficient proportionality constant for individual VOCs. The value of ψ can be measured. However, it is more common to estimate its value based on compound diffusivities such that

$$\psi = \left\{\frac{D_{voc}}{D_{O_2}}\right\}^n,$$ (12)

where D_{voc} and D_{O_2} are liquid molecular diffusion coefficients for a VOC and oxygen, respectively (m^2/s), and n is an exponent ranging from 0.5 (for penetration and surface renewal theories) to 1.0 (for two-film theory). Measured values of ψ have been noted to be approximately 0.6 for many VOCs in well-mixed aqueous systems (Roberts et al. [18]).

For applications of VOC transfer across wastewater surfaces adjacent to open atmospheres, C_g is assumed to be small and Equation (10) reduces to

$$R_v = -k_lC_lA,$$ (13)

thus reducing the sensitivity of mass transfer to H_c. However, Equation (13) can lead to significant overestimation of emissions for covered processes or rising air bubbles that accumulate VOCs in the gas phase. Each system requires complete application of Equation (10), with an appropriate mass balance on the gaseous phase.

If it is assumed that air bubbles become saturated with a VOC during transport through wastewater, stripping losses can be estimated by

$$R_v = -Q_gC_lH_c,$$ (14)

where Q_g is forced aeration rate (m^3/s), and the product C_lH_c is equal to the saturation gas concentration, i.e. in equilibrium with the surrounding liquid. This may be a poor approximation for highly volatile VOCs for which air bubbles reach only partial saturation during rise through wastewater. For such conditions and the assumption that bubble size remains constant, Equation (14) can be modified to

$$R_v = -Q_gC_lH_c\left\{1 - \exp\left(\frac{-\psi k_oV}{H_cQ_g}\right)\right\},$$ (15)

where the term in brackets was described by Roberts et al. [18] and accounts for degree of saturation, and k_o is a system-specific oxygen transfer coefficient (1/s). All other variables

are as previously defined. Note that for a given aeration rate and reactor volume, the degree of saturation approaches unity as H_c becomes small, and may be significantly less than 1.0 for higher volatility VOCs such as carbon tetrachloride, tetrachloroethene, and vinyl chloride.

For volatilization at drop structures, it is not possible to accurately quantify interfacial contact area, i.e. for droplets formed by falling water contact with an underlying receiving water. Thus, models to estimate VOC emissions from drop structures are empirical, and rely on relationships associated with oxygen absorption at such structures. Equations developed to predict mass transfer for falling streams have focused on oxygen transfer to clean water flowing over weirs. Existing equations rely on regression analyses using laboratory or field data to correlate drop height, discharge, and pool depth to the dimensionless ratio

$$r_{O_2} = \left\{ \frac{C_s - C_1}{C_s - C_2} \right\}, \tag{16}$$

where r_{O_2} is referred to as the deficit or depletion ratio, and C_s, C_1, and C_2 are saturation, upstream, and downstream dissolved oxygen concentrations (mg/m^3), respectively.

The value of r_{O_2} is related to an analogous term for VOCs according to

$$r_{voc} = r_{O_2}{}^{\alpha\psi}, \tag{17}$$

where α is a transfer coefficient ratio between wastewater and tap water, and ψ is described by Equation (12). For a system with a well-mixed gas phase, the term r_{voc} is equal to

$$r_{voc} = \frac{C_{1\text{-}voc} - \dfrac{C_g}{H_c}}{C_{2\text{-}voc} - \dfrac{C_g}{H_c}}, \tag{18}$$

where $C_{1\text{-}voc}$ and $C_{2\text{-}voc}$ are VOC concentrations immediately upstream and downstream of the drop (mg/m^3), respectively. Rearranging Equation (18) leads to

$$C_{2\text{-}voc} = \frac{C_{1\text{-}voc}}{r_{voc}} + \frac{C_g}{H_c} \left\{ 1 - \frac{1}{r_{voc}} \right\}, \tag{19}$$

so that an increase in r_{voc} leads to a decrease in $C_{2\text{-}voc}$ and associated increase in VOC emissions. If the drop structure is open to the atmosphere and well-ventilated, C_g can be assumed to be negligible and Equation (19) reduces to

$$C_{2\text{-}voc} = \frac{C_{1\text{-}voc}}{r_{voc}}. \tag{20}$$

Otherwise, the second term in Equation (19) must be retained to account for retardation of mass transfer by VOC accumulation in the gas phase above falling wastewater.

Several researchers have developed empirical relationships for r_{O_2}. Gameson [7] studied oxygen transfer over river structures, and Amy and Novak [1] completed extensive experimental work to analyze oxygen transfer caused by flow over weirs. Nakasone [11] was the first to develop an equation that incorporates receiving pool depth and effects of entrained air bubbles in the receiving pool. Pincince [17] was the first to develop an oxygen transfer equation based on dissolved oxygen measurements upstream and downstream of primary and secondary clarifier weirs. Multiple linear regressions were completed to determine best-fit coefficients, assuming a relationship similar in form to Nakasone's model. The form of Pincince's and Nakasone's models is

Table 1 Coefficients for Nakasone and Pincince models.

h (m)	q(m^3/h-m)	W	ϵ	b	j
<1.2	<235	0.0785	1.31	0.428	0.31
>1.2	<235	0.0861	0.816	0.428	0.31
<1.2	>235	5.39	1.31	−0.363	0.31
<1.2	>235	5.92	0.816	−0.363	0.31
Pincince—primary		0.0482	0.872	0.509	0.00
Pincince—secondary		0.077	0.623	0.66	0.00

$$ln(r_{O_2}) = Wh^\epsilon\theta^b y^j, \tag{21}$$

where h is drop height (m), q is discharge per meter width of weir at the water surface (m^2/hr), y is tailwater depth (m), and W, ϵ, b, and j are empirical coefficients as listed in Table 1. Unlike the Nakasone model, Pincince's model should not require an α factor because of its derivation from field experiments in operating treatment systems. Furthermore, the Pincince model was observed to be insensitive to tailwater depth. Pincince [17] noted that wastewater often trickles down the weir trough wall to the underlying receiving water, unlike the free-fall conditions described by Nakasone [11].

THE BASTE MODEL

As a response to air toxics legislation in California, a consortium of POTWs pooled resources to form the San Francisco Bay Area Air Toxics (BAAT) group. An important objective of BAAT was to develop a multi-process computer-based GFM with the flexibility to simulate VOC emissions from liquid processes at any POTW in the consortium. This resulted in a novel Bay Area Sewage Toxics Emissions model (BASTE).

The BASTE model allows the use of five model "building blocks" to simulate the fate of VOCs in individual treatment processes. Building block options include:
1. series of continuous flow stirred tank reactors with multiple options to describe aeration
2. quiescent surfaces
3. drop structures
4. packed-media systems
5. measured emissions or prescribed emission factors.

Thus, a primary clarifier can be simulated as a quiescent surface followed in series by an effluent drop (weir), and so on. The BASTE model allows for building blocks to be placed in series or parallel. Building blocks are connected by links which may themselves be considered blocks from which VOC emissions can occur, e.g. aerated conveyance channels. Wastewater flows are directed from the effluent of one block to the influent of another by user-prescribed fractions of total flow into a plant. In this way, a block may receive influent from several other blocks, including downstream blocks, i.e. recycle. The building block approach gives BASTE the flexibility to simulate thousands of treatment configurations.

Each block in a treatment process can be covered, and the mathematical equations used to estimate VOC emissions account for mass balances in the gas phase. Thus, each block is characterized by an equation reflecting mass balances in both the liquid and gas phases, and requires knowledge of block influent concentrations (calculated as combined effluent concentrations from relevant input blocks) for each VOC. An explicit solution is used to solve the resulting set of equations, and an iterative algorithm is used to solve for the effects of recycle flows.

A description of the mathematical development of each building block is provided below.

Block I—Series of CFSTRs

A steady-state mass balance on a well-mixed reactor can be expressed as

$$QC_{li} - QC_l + R_s + R_b + R_v = 0, \qquad (22)$$

where Q is wastewater flow rate (m^3/s) through the reactor, C_{li} and C_l are VOC concentrations in the liquid influent and reactor/effluent streams (mg/m^3), respectively, Q_w is sludge wastage flow rate (m^3/s), and R_s, R_b, and R_v are as described previously.

Equations (1) and (2) are used to model adsorption losses. Liquid-solid partition coefficients are estimated using Equation (3a) and Equation (3b) or Equation (6). Thus, R_s is expressed as

$$R_s = -\phi C_l, \qquad (23)$$

where

$$\phi = 6.3 \times 10^{-7} \gamma K_{ow} Q_w X, \text{ or} \qquad (24)$$

$$\phi = \gamma Q_w X 10^{0.58 \log(Kow) + 1.14} \qquad (25)$$

Biodegradation is modeled as first-order in VOC and active cell concentrations. Thus, Equation (8) is used and R_b is expressed as

$$R_b = -BC_l, \qquad (26)$$

where

$$B = k_1 X_a V. \qquad (27)$$

The model utilizes literature-based k_1 values. For several compounds, a conservative (in terms of emissions) assumption is made that $k_1 = 0.0$. The BASTE model allows the user to change k_1 values for any compound. This is an important feature of BASTE since k_1 is likely to vary between systems, and can be obtained through tracer studies, e.g. in operating activated sludge systems.

The volatilization rate R_v is expressed as the sum of three components such that

$$R_v = R_{v,n} + R_{v,s} + R_{v,b}, \qquad (28)$$

where $R_{v,n}$ represents volatilization from non-agitated surfaces, e.g. non-aerated channel surfaces, $R_{v,s}$ represents volatilization caused by mechanical surface aeration, and $R_{v,b}$ represents volatilization caused by mass transfer to rising air bubbles.

The term $R_{v,n}$ is modeled according to Equation (10). The liquid-phase transfer coefficient is obtained by Equation (11), and one of two options to estimate k_{l,O_2}. The first is based on a model presented by Parkhurst and Pomeroy [15] for oxygen transfer in untreated wastewater,

$$k_{l,O_2} = 2.67 \times 10^{-4}(1 + 0.17F^2)(SU)^{3/8}, \qquad (29)$$

where k_{l,O_2} has units of m/s, F is the Froude number, S is the slope of the energy grade line (m/m), and U is wastewater mean velocity (m/s). If the slope of the energy grade line is not known, k_{l,O_2} is estimated using a model developed by O'Connor and Dobbins [13] and adjusted for applications to wastewater.

$$k_{l,O_2} = \alpha 4.86 \times 10^{-5} U^{0.5} d^{-0.5}, \qquad (30)$$

where d is mean hydraulic depth (m), and all other terms are as described previously.

For systems which utilize mechanical surface aeration, Equations (10) and (11) are used with k_{l,O_2} (m/s) estimated by

$$k_{l,O_2} = \frac{N_c P}{3600 A_a C^*}, \qquad (31)$$

where N_c is oxygen transfer rate per surface aerator (kg O_2/KW-hr), P is brake power per aerator (KW), A_a is reactor surface area divided by number of aerators (m^2), and C^* is the oxygen saturation concentration at a specific temperature and barometric pressure (Roberts et al. [18]).

Equation (15) is used to estimate emissions caused by diffused bubble aeration. Thus,

$$R_{v,b} = -\gamma C_l, \qquad (32)$$

where

$$\gamma = \left\{ 1 - exp\left(\frac{-\psi k_o V}{H_c Q_g} \right) \right\} Q_g H_c. \qquad (33)$$

To account for VOC accumulation in the gas phase, an assumption is made that all liquid processes exist under a hypothetical bubble which may represent a physical cover. If steady-state conditions are assumed, a mass balance on the gas volume yields

$$Q_v C_a - Q_v C_g + k_{l,n}\left(C_l - \frac{C_g}{H_c} \right) A$$
$$+ k_{l,s}\left(C_l - \frac{C_g}{H_c} \right) + \gamma C_l = 0, \quad (34)$$

where Q_v is gas ventilation rate (m^3/s), and C_a is ambient VOC concentration (mg/m^3). If C_a is assumed to be zero, Equation (34) can be solved for C_g to yield

$$C_g = K_D C_l, \qquad (35)$$

where

$$K_D = \frac{(k_{l,n}A + k_{l,s}A + \gamma)}{\left(Q_v + k_{l,n}\dfrac{A}{H_c} + k_{l,s}\dfrac{A}{H_c} \right)}. \qquad (36)$$

Equation (36) indicates that if Q_v is large, K_D becomes very small and C_g approaches zero. This is the so called infinite dilution assumption that is made for unconfined processes modeled using other GFMs.

Equations (23) through (36) can be rearranged to yield

$$C_l = \frac{C_{li}}{\left\{ 1 + \dfrac{Q_w}{Q} + \dfrac{\phi}{Q} + \dfrac{B}{Q} + \left[1 - \dfrac{K_D}{H_c} \right](k_{l,n} + k_{l,s})\dfrac{A}{Q} + \dfrac{\gamma}{Q} \right\}}. \qquad (37)$$

Equation (37) is applicable to process blocks which are modeled as a single CFSTR. It can be used repeatedly to simulate a series of CFSTRs, i.e. with C_l from one CFSTR serving as C_{li} to the next, but only if Q_v is so large that K_D and C_g are negligible, i.e. infinite dilution. This constraint exists since the

mass balance on the gas phase is based on an assumption that a well-mixed gas concentration exists above a uniform liquid concentration.

The value of C_l obtained for each CFSTR can be substituted back into Equations (10), (15), (23), (26), and (28) to obtain mass losses from wastewater due to volatilization, biodegradation, and adsorption.

Building Block II—Quiescent Surfaces

Most models of emissions from quiescent surfaces are based on the assumption that the underlying liquid is well-mixed. That assumption was also made in the development of BASTE. Thus, a quiescent surface is modeled as a single CFSTR. If biodegradation and adsorption are assumed to be negligible, and surface and bubble aeration are neglected for quiescent surfaces, Equation (37) simplifies to

$$C_l = \frac{C_{li}}{\left\{ 1 + \frac{Q_w}{Q} + k_{l,n} \frac{A}{Q} \left[1 - \frac{K_D}{H_c} \right] \right\}}. \tag{38}$$

To estimate $k_{l,n}$, the BASTE model utilizes results of studies published by Cohen et al. [5] for volatilization of benzene and toluene from liquid baths placed in a wind tunnel. The value of $k_{l,n}$ was observed to correlate well with wind speed at 10 cm above the liquid surface, U_{10}. For values of U_{10} less than 3 m/s, $k_{l,n}$ was relatively insensitive to U_{10}, with a value of 8×10^{-6} m/s. For U_{10} between 3 and 10 m/s, $k_{l,n}$ was empirically related to the roughness Reynolds number, with values of 8×10^{-6} m/s and 8×10^{-5} m/s for $U_{10} = 3$ m/s and 10 m/s, respectively. Values of $k_{l,n}$ for VOC i are estimated in BASTE by multiplying $k_{l,n}$ for benzene by $\psi_i/\psi_{benzene}$. Volatile emissions from quiescent surfaces are estimated by substituting Equation (38) into Equation (10).

Building Block III—Drop Structures

Volatilization is assumed to be the only fate mechanism for VOCs at drop structures. Equations (16) through (19) are used to estimate VOC concentration reductions across weirs and other drops. Volatile emissions are then estimated by

$$E_v = (C_{1\text{-}voc} - C_{2\text{-}voc}) Q, \tag{39}$$

where E_v is emission rate (mg/s), and all other terms are as defined previously.

There are several options for obtaining r_{O_2} for use in Equation (17). The BASTE model allows estimation of oxygen transfer at weirs using Nakasone's [11] model for free falling drop structures, or Pincince's [17] equations for primary or secondary clarifier weirs. Alternately, measured dissolved oxygen concentrations and temperatures can be used for direct substitution into Equation (16). The BASTE model calculates C_s based on input temperature and an assumed barometric pressure of one atmosphere.

For covered drop structures a bubble concept similar to the one described for CFSTRs is used. A steady-state mass balance on an enclosed gas space above drops leads to

$$Q_v C_a - Q_v C_g + (C_{1\text{-}voc} - C_{2\text{-}voc}) Q = 0, \tag{40}$$

where the gas-phase generation term is simply the mass lost from liquid. It is further assumed that C_a is negligible with respect to C_g, allowing Equation (40) to be rewritten as

$$C_g = (C_{1\text{-}voc} - C_{2\text{-}voc}) \frac{Q}{Q_v}. \tag{41}$$

Substitution of Equation (41) into Equation (19) yields

$$C_{2\text{-}voc} = \frac{\dfrac{C_{1\text{-}voc}}{r_{voc}} - \dfrac{C_{1\text{-}voc} Q}{H_c Q_v} \left[\dfrac{1}{r_{voc}} - 1 \right]}{1 - \dfrac{Q}{H_c Q_v} \left[\dfrac{1}{r_{voc}} - 1 \right]}. \tag{42}$$

Thus, if Q_v becomes large, $C_{2\text{-}voc}$ approaches $C_{1\text{-}voc}/r_{voc}$. This is a typical assumption for mass transfer to and from falling liquids. However, the BASTE model allows for the more general condition of gas accumulation, given the assumption of a well-mixed drop head space.

Building Block IV—Packed-Media Systems

Processes involving packed media include ammonia stripping towers and trickling filters. The former is generally characterized by stripping as the only removal mechanism. The latter may include sorption and biodegradation. However, there is a paucity of information related to biodegradation of VOCs in trickling filters. Thus, BASTE uses an assumption that volatilization is the dominant removal mechanism for all VOCs in any type of packed media system. For trickling filters, this is a conservative assumption for VOCs which are considered to be aerobically degradable. However, it may not lead to significant errors in emissions estimates for aerobically recalcitrant VOCs. Furthermore, equations to estimate VOC emissions can still be used to assess relative changes in VOC emissions with changes in process operating parameters.

Both counter-current (gas and liquid flowing in opposite directions) and co-current (gas and liquid flowing in the same direction) systems may occur. A simple mass balance equating liquid VOC loss to gaseous VOC gain leads to

$$Q(C_{l1} - C_{l2}) = Q_g(C_{g1} - C_{g2}) \quad \text{(counter current)}, \tag{43}$$

and

$$Q(C_{l1} - C_{l2}) = Q_g(C_{g2} - C_{g1}) \quad \text{(co-current)}, \tag{44}$$

where the subscripts 1 and 2 refer to the physical top and bottom of the packed media system, respectively. The terms Q and Q_g refer to liquid and gas flow rates (m³/s), respectively, and C_l and C_g are aqueous and gaseous VOC concentrations (mg/m³).

If the inlet gas is assumed to contain negligible quantities of VOCs, Equations (43) and (44) reduce to

$$Q(C_{l1} - C_{l2}) = Q_g C_{g1} \quad \text{(counter current)}, \tag{45}$$

and

$$Q(C_{l1} - C_{l2}) = Q_g C_{g2} \quad \text{(co-current)}. \tag{46}$$

The BASTE model utilizes a conservative assumption to solve Equations (45) and (46). It is assumed that VOCs in the effluent gas stream exist in thermodynamic equilibrium with VOCs in the adjacent wastewater stream. Thus,

$$C_{g1} = H_c C_{l1} \quad \text{(counter current)}, \tag{47}$$

and

$$C_{g2} = H_c C_{l2} \quad \text{(co-current)}. \tag{48}$$

Substitution of Equations (47) and (48) into Equations (45) and (46) leads to

$$C_{l2} = \left[1 - \frac{Q_g H_c}{Q} \right] C_{l1} \quad \text{(counter current)}, \qquad (49)$$

and

$$C_{l2} = \frac{Q C_{l1}}{Q + Q_g H_c} \quad \text{(co-current)}. \qquad (50)$$

Since volatilization is assumed to be the only loss mechanism, the BASTE model estimates emissions as the product of Q and $(C_{l1} - C_{l2})$.

Building Block V—Measured Emissions and Emission Factors

The BASTE model includes a fifth building block that allows for measured emissions of individual VOCs, or emission and removal factors for processes that BASTE is not otherwise capable of simulating. Emission factors are defined as the fraction of VOC mass inflow that is emitted to the atmosphere, f_e. Removal factors are defined as the fraction of VOC mass inflow that is lost due to the sum contribution of all mechanisms, f_r. Thus,

$$f_e < f_r. \qquad (51)$$

If emission and removal factors are used, emissions for a specific process are estimated as

$$E_v = f_e Q C_{li}. \qquad (52)$$

Concentrations in the process effluent stream are estimated as

$$C_l = (1 - f_r) C_{li}. \qquad (53)$$

If known emission rates (E_v) are prescribed for a specific block, the effluent concentration for the block is estimated by equating

$$Q(C_{li} - C_l) = \frac{f_r}{f_e} E_v, \qquad (54)$$

and solving for C_l such that

$$C_l = C_{li} - \frac{f_r E_v}{f_e Q}. \qquad (55)$$

Thus, Equations (53) and (55) override modeled emissions estimates, and the BASTE model allows an integration of mathematical model estimates with measured VOC emissions.

A summary of several important features of the BASTE model is provided below:

1. The model allows for retardation of mass transfer by gas accumulation in covered treatment processes. This requires simultaneous solution of mass balances in the aqueous and gaseous phases.
2. The BASTE algorithm has the ability to simulate recycle flows from any number of downstream processes to any number of upstream processes, including split recycles.
3. The BASTE model is not constrained to pre-specified process algorithms without the flexibility to handle variations in treatment processes. Instead, it will simulate processes based on four primary building blocks: 1) series of continuous-flow stirred tank reactors, 2) quiescent surfaces, 3) drops or weirs, and 4) packed-media systems.
4. The BASTE model allows a mix of emissions compu-

tations and measured emission rates. Similarly, BASTE allows for the use of emission factors in place of mechanistic computations.
5. The BASTE model allows for any number of building blocks in series or parallel. Mass flows are directed from one block to another by specifications on a menu-driven input screen.
6. The BASTE model allows the use of measured changes in dissolved oxygen concentrations across weirs and drops. If such data are used, they override model estimates of VOC losses from drops and weirs, and theoretically relate VOC desorption to measured oxygen absorption.
7. The BASTE model has an option which allows adjustment of computational results to meet measured effluent concentrations. This requires iterations over the entire WWTF for each VOC, and is an effective plant-specific calibration method that is completed during model execution.

BASTE EVALUATION

Evaluation of the BASTE model is a continuing process as field data become available. A preliminary evaluation has been completed using aqueous and gaseous field data acquired from eight wastewater treatment facilities in the San Francisco Bay Area. The BASTE model was executed using process operating parameters and influent VOC concentrations for each detected VOC.

Figure 1 is a plot of measured versus modeled fractional removal of VOCs across entire treatment facilities. The data stem from influent and effluent monitoring at eight WWTFs, and include BASTE simulations for trichloroethene (TCE), tetrachloroethene, chloroform, toluene, and total xylenes. The line drawn through the data is a 1:1 fit, and not a least-squares fit. The correlation coefficient (R) for the measured and modeled removal values is 0.89, and is as high as 0.95 if the worst outlier (1) is omitted.

Figure 1 provides some insight as to the BASTE model's ability to simulate losses from entire liquid treatment trains. However, it does not indicate whether losses are attributed to volatilization, sorption, or biodegradation. Few direct emissions measurements have been made at the WWTFs which were studied. However, limited gas-phase sampling was completed at two WWTFs that have several covered processes. Figure 2 is a plot of measured versus modeled emissions at plant headworks, primary treatment processes, and secondary treatment processes for benzene, carbon tetrachloride, methylene chloride, toluene and total xylenes. The data set is relatively sparse and similar comparisons are intended as more data become available. The R value associated with data plotted in Figure 2 is 0.92. When the data were separated into headworks (including grit chambers), primary treatment, and secondary treatment, regression analyses led to R values of 0.96, 0.93, and 0.71, respectively, with the caveat that as few as four data points were available for the headworks. The worst results were for activated sludge systems, which reflects high uncertainties associated with extrapolating literature-based k_1 values to operating activated sludge treatment plants. Model performance for carbon tetrachloride and methylene chloride was much better than for the non-halogenated aromatic VOCs, reflecting low degradability ($k_1 = 0.0$ assumed for the former) for the halogenated compounds.

APPLICATIONS OF GENERAL FATE MODELS

General fate models can be used to estimate VOC emissions for 1) air toxics or reactive organic gas (ROG) emissions inventories, 2) input to atmospheric transport models used for
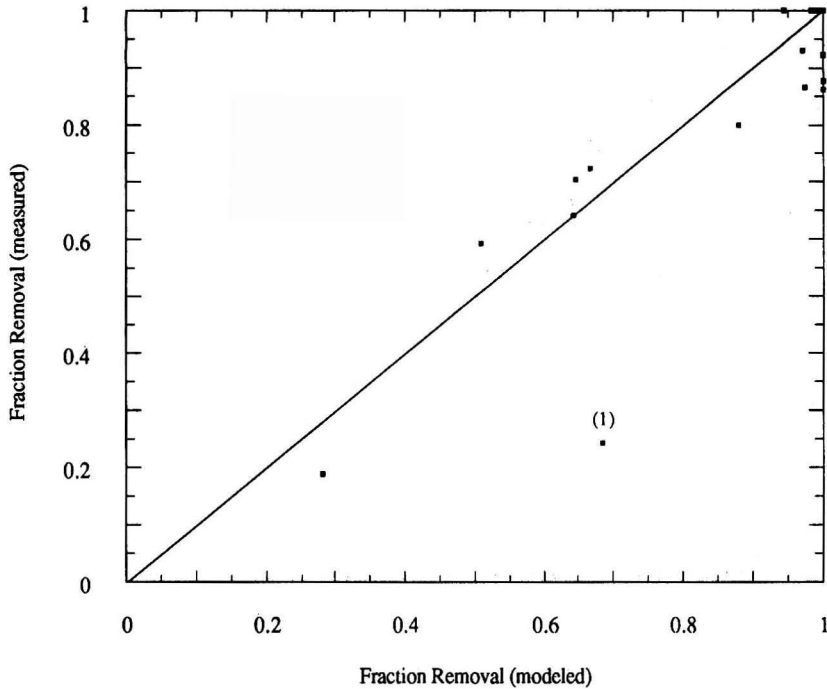
FIGURE 1. Measured versus modeled fractional removal across WWTFs.

risk assessments, and 3) investigations of the feasibility of reducing VOC emissions by simple process modifications. The BASTE model has been used to predict emissions from over 30 wastewater treatment facilities in California, Washington, Wisconsin, and New Jersey. Furthermore, O'Neill et al. [14] used BASTE to analyze the effects of process modifications on VOC emissions from nine WWTFs in the San Francisco Bay Area. These analyses focused on methods for keeping
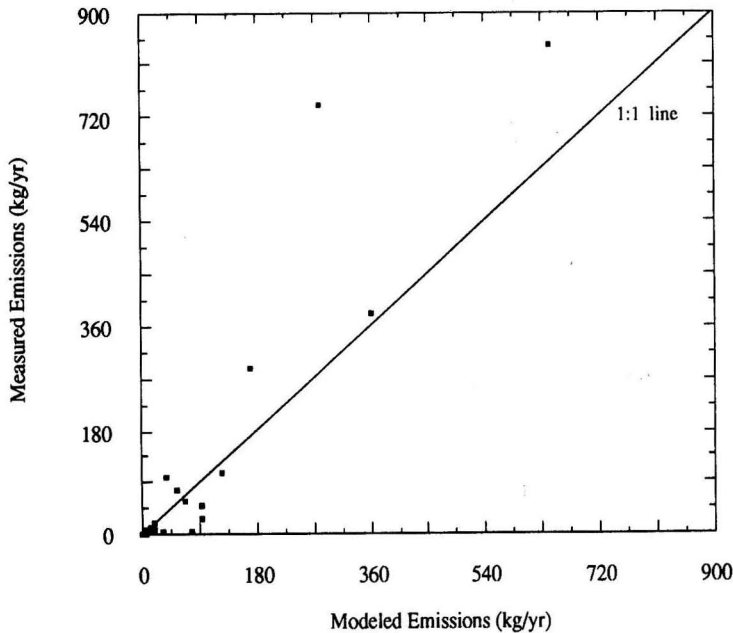
FIGURE 2. Measured versus modeled VOC emissions at eight WWTFs.

degradable compounds in solution during primary treatment, and for isolating emissions of recalcitrant compounds at one location for more efficient gas-phase control.

SUMMARY

This paper provides a review of existing methods to estimate VOC emissions from wastewater. Volatilization, biodegradation, and adsorption to solid particles and biomass were described as predominant mechanisms affecting the fate of VOCs during wastewater treatment. With proper evaluations using a growing base of field data, confidence in the accuracy of GFMs will increase and improved GFMs can be derived. Such models will likely play an important role in predicting VOC emissions from industrial and municipal wastewater treatment facilities.

A new GFM (BASTE) was presented in this paper. Derivations and a preliminary evaluation of the BASTE model were described. The BASTE model has several features which make it useful for estimating VOC emissions and the feasibility of process modifications as a VOC control strategy. The most important feature of the BASTE model is its flexibility and ability to simulate thousands of treatment configurations using a novel building block approach. The BASTE model is intended to evolve as additional data become available to refine biological rate constants and specific building block algorithms.

NOTATION

A = Interfacial surface area between gas and liquid (m^2)
A_a = Reactor surface area per aerator (m^2)
b = Empirical coefficient for drop models
C^* = Saturation dissolved oxygen concentration (mg/m^3)
C_1 = Dissolved oxygen concentration upstream of a drop (mg/m^3)
$C_{1\text{-}voc}$ = VOC concentration in wastewater upstream of a drop (mg/m^3)
C_2 = Dissolved oxygen concentration downstream of a drop (mg/m^3)
$C_{2\text{-}voc}$ = VOC concentration in wastewater downstream of a drop (mg/m^3)
C_a = Ambient air concentration of a VOC (mg/m^3)
C_g = Gaseous VOC concentration (mg/m^3)
G_{g1} = VOC concentration in the gas phase at the top of a packed-media system (mg/m^3)
C_{g2} = VOC concentration in the gas phase at the bottom of a packed-media system (mg/m^3)
C_l = VOC concentration in wastewater in a well-mixed reactor (mg/m^3)
C_{t1} = VOC concentration in wastewater at the top of a trickling filter (mg/m^3)
C_{t2} = VOC concentration in wastewater at the bottom of a trickling filter (mg/m^3)
C_{li} = VOC concentration in a wastewater influent stream (mg/m^3)
C_s = Saturation dissolved oxygen concentration (mg/m^3)
d = Mean hydraulic depth (m)
D_{O_2} = Molecular diffusion coefficient for oxygen in wastewater (m^2/s)
D_{voc} = Molecular diffusion coefficient for VOC in wastewater (m^2/s)
E_v = Emission rate (mg/s)
f_e = Fraction of VOC mass influent emitted to atmosphere
f_r = Fraction of VOC mass influent lost due to sum contribution of all fate mechanisms
F = Froude number

g = Fraction of solid mass accounted for by organic carbon
h = Fall height (m)
H_c = Dimensionless Henry's law constant
j = Empirical coefficient for drop models
k = Maximum specific substrate utilization (mg/mg-VSS·s)
k_1 = Effective first-order biological rate constant (m^3/mg-VSS·s)
k_l = Liquid-phase transfer coefficient (m/s)
$k_{l,n}$ = VOC liquid-phase transfer coefficient for non-agitated surfaces (m/s)
k_{l,O_2} = Liquid-phase transfer coefficient for oxygen (m/s)
$k_{l,s}$ = VOC liquid-phase transfer coefficient for surface aerators (m/s)
$k_{l,voc}$ = Liquid-phase transfer coefficient for VOCs (m/s)
k_o = Oxygen transfer coefficient (1/s)
K_D = Finite ventilation adjustment factor
K_l = Overall gas-liquid mass transfer coefficient (m/s)
K_{ow} = Octanol/water partition coefficient
K_p = Liquid-solid partition coefficient (volume/mass organic solids)—varied units
K_p' = Liquid-solid partition coefficient (volume/mass solids)—varied units
K_s = Monod half-velocity constant (mg/m^3)
N_c = Oxygen transfer rate per surface aerator (kg O_2/kW-hr)
P = Brake power per aerator (kW)
q = Mass of contaminant sorbed per mass of solids (mg/mg)
Q = Wastewater flow rate (m^3/s)
Q_g = Forced aeration rate (m^3/s)
Q_v = Head space ventilation rate (m^3/s)
Q_w = Wasted sludge flow rate (m^3/s)
r_{O_2} = Oxygen deficit ratio
r_{voc} = VOC deficit ratio
R_b = Mass rate of biodegradation (mg/s)
R_s = Rate of VOC removal to sludge streams (mg/s)
R_v = Rate of volatile emissions (mg/s)
$R_{v,b}$ = Rate of stripping caused by diffused air bubbles (mg/s)
$R_{v,n}$ = Rate of volatilization from non-agitated surfaces (mg/s)
$R_{v,s}$ = Rate of volatilization caused by mechanical surface aeration (mg/s)
S = Slope of the energy grade line (m/m)
U = Wastewater mean velocity (m/s)
U_{10} = Wind speed 10 cm above a wastewater surface (m/s)

LITERATURE CITED

1. Avery, S. T., and P. Novak, "Oxygen Transfer at Hydraulic Structures," *Journal of the Hydraulics Division*, ASCE, **104**: 1521 (1978).
2. Barton, D. A., "Intermedia Transport of Organic Compounds in Biological Wastewater Treatment Processes," *Environmental Progress*, **6**(4): 246 (1987).
3. Blackburn, J. W., "Prediction of Organic Chemical Fates in Biological Treatment Systems," *Environmental Progress*, **6**(4): 217 (1987).
4. Chang, D. P. Y., E. D. Schroeder, and R. L. Corsi, "Emissions of Volatile and Potentially Toxic Organic Compounds from Sewage Treatment Plants and Collection Systems," A5-127-32, California Air Resources Board, Sacramento (1987).
5. Cohen, Y., W. Cocchio, and D. Mackay, "Laboratory Study of Liquid-Phase Controlled Volatilization Rates in Presence of Wind Waves," *Environ. Sci. Technol.*, **12**(5): 553 (1978).

6. Dobbs, R. A., L. Wang, and R. Govind, "Sorption of Toxic Organic Compounds on Wastewater Solids: Correlation with Fundamental Properties," *Environ. Sci. Technol.*, **23**(9): 1092 (1989).

7. Gameson, A. L. H., "Weirs and the Reaeration of Rivers," *Journal of the Institute of Water Engineers*, **11**, 477 (1957).

8. Govind, R., L. Lei, and R. Dobbs, "Integrated Model for Predicting the Fate of Organics in Wastewater Treatment Plants," *Environmental Progress*, **10**(1): 13 (1991).

9. Karickhoff, S. W., D. S. Brown, and T. A. Scott, "Sorption of Hydrophobic Pollutants on Natural Sediments," *Water Research*, **13**, 241 (1979).

10. Matter-Muller, C., W. Gujer, and W. Giger, "Transfer of Volatile Substances from Water to the Atmosphere," *Water Research*, **15**, 1271 (1981).

11. Nakasone, H., "Study of Aeration at Weirs and Cascades," *Journal of Environmental Engineering*, ASCE, **113**(1): 64 (1986).

12. Namkung, E., and B. E. Rittmann, "Estimating Volatile Organic Compound Emissions From Publicly Owned Treatment Works," *Journal of the Water Pollution Control Federation*, **59**(7): 670 (1987).

13. O'Connor, D. J., and W. E. Dobbins, "Mechanisms of Reaeration in Natural Streams," *Transactions*, ASCE, **123**(2934): 641 (1958).

14. O'Neill, K., R. L. Corsi, and T. R. Card, "Process Modifications to Reduce VOC Emissions from Wastewater," *Proceedings of the 84th Annual Meeting of the Air and Waste Management Association*, Vancouver (1991).

15. Parkhurst, J. D., and R. D. Pomeroy, "Oxygen Absorption in Streams," *Journal of the Sanitary Engineering Division*, ASCE, **98**(SA1): 101 (1972).

16. Petrasek, A. C., B. M. Austern, and T. W. Neiheisel, "Removal and Partitioning of Volatile Organic Priority Pollutants in Wastewater Treatment," in *Proceedings of the 9th U.S.-Japan Conference on Sewage Treatment Technology*, Tokyo (1983).

17. Pincince, A. B., "Transfer of Oxygen and Emissions of Volatile Organic Compounds at Clarifier Weirs," *Research Journal of the Water Pollution Control Federation*, **63**(2): 114 (1991).

18. Roberts, P. V., P. Dandliker, and C. Matter-Muller, "Volatilization of Organic Pollutants in Wastewater Treatment—Model Studies," EPA-600/2-84-047, U.S. Environmental Protection Agency, Cincinnati (1984).

19. Smith, J. H., D. C. Bomberger, and D. L. Haynes, "Prediction of the Volatilization Rates of High-Volatility Chemicals from Natural Water Bodies," *Environ. Sci. Technol.*, **14**(1): 1332 (1980).

20. Tsezos, M., and J. P. Bell, "Comparison of the Biosorption and Desorption of Hazardous Organic Pollutants by Live and Dead Biomass," *Water Research*, **23**(5): 561 (1989).

21. Tsivoglou, E. C., R. L. O'Connell, C. M. Walter et al., "Tracer Measurements of Atmospheric Reaeration—I. Laboratory Studies," *Journal of the Water Pollution Control Federation*, **37**(10): 1343 (1965).

22. Weber, W. J., and B. E. Jones, "Toxic Substance Removal in Activated Sludge and PAC Treatment Systems," *1984 Annual Conference of the Water Pollution Control Federation*, New Orleans (1984).

Control of Aromatic Waste Air Streams by Soil Bioreactors

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Three soils were examined for the ability to degrade hydrocarbon vapors of benzene, toluene, ethylbenzene, and o-xylene (BTEX). Each of these compounds are major aromatic constituents of gasolines. The soils examined were Rubicon Sand from Traverse City, Michigan, Durant Loam from Ada, Oklahoma, and Dougherty Sand from Stratford, Oklahoma. Soil columns were used to examine the effects of soil type, air flow rate and inlet vapor concentrations. Adjustment of the hydrocarbon loading rate produced removals which corresponded to first-order removal kinetics. Estimated residence times of 10 to 20 minutes produced removals of the individual inlet BTEX compounds which ranged from 8 to 39%. Increasing the residence time produced increased removals corresponding to first-order removal rates. Further increases in the residence time revealed transport limitations which restricted additional removals. Soil which had moisture less than 50% of saturation displayed preferential utilization of benzene followed in order by ethylbenzene, toluene, and o-xylene.

INTRODUCTION

Contamination of groundwater resources is a serious environmental problem which is continuing to increase in occurrence in the United States. It has been reported that leaking underground gasoline storage tanks may pose the most serious threat of all sources of groundwater contamination [1]. Gasolines are comprised of a variety of aliphatic and aromatic hydrocarbons. The aromatic portion consists primarily of benzene, toluene, ethylbenzene, and xylenes (BTEX compounds). BTEX compounds are also among the most frequency identified substances at Superfund sites [2]. Pump and treat well systems are the most common and frequently used technique for aquifer restoration. Treatment is often in the form of air stripping to remove the volatile components from the contaminated water [3]. Additionally, soil ventilation processes have been used to remove volatile components from the vadose zone [4]. Both air stripping and soil ventilation produce a waste gas stream containing volatile compounds which is normally treated by carbon adsorption or incineration. Both treatment processes require a substantial capital investment and continual operation and maintenance expenditures.

The objective of this study was to examine the potential of using soil bioreactors to treat a waste gas stream produced by an air stripping or soil ventilation process. Previous studies have been shown that various hydrocarbons can be successfully treated with soils [5, 6, 7, 8]. This study examined the removal of BTEX compounds within soil columns and the influence of soil type, inlet concentration, and inlet flow rate on the removal efficiency.

MATERIALS AND METHODS

Chemicals

The chemicals used in the soil bioreactors project were Baker spectrophotometric grade benzene, Baker reagent grade to-

FIGURE 1. Soil column apparatus.

gathering the individual vapors into one stream to be directed into the bottom of the soil column. Figure 1 shows a schematic of the soil column apparatus. Air was pumped through the vials with a Technicon Autoanalyzer pump and the rate was controlled by use of appropriate sized pump tubing. Tubing was replaced once a week. All lines were made of Technicon pump tubing or Teflon tubing.

Methods of Analysis

The hydrocarbon vapor stream was sampled at the inlet and the outlet of each soil column. Samples were collected onto Tenax traps. Each trap consisted of a 0.64 cm by 10 cm stainless steel tube which contained five cm of 60/80 mesh Tenax held in place with glass wool plugs. Hydrocarbon removal was determined by comparison of the inlet and outlet concentrations. Flow rates were measured prior to each sampling period.

Sample analysis was performed using a Varian 3700 gas chromatograph. The Varian 3700 was equipped with a flame ionization detector and a 0.32 cm by 182.9 cm stainless steel packed column containing 5% SP-1200/1.75% Bentone 34 on 100/120 Supelcoport. Nitrogen (N_2) was used as the carrier gas at 40 ml/min and the operating temperatures for the injector and detector were 170°C and 180°C, respectively. The column temperature was programmed for an initial temperature of 50°C for 1 min, ramp 8°C/min to 130°C, and hold for 1 min. A Tekmar LSC-2 was used to add an internal standard to each sample prior to desorbing onto the Varian 3700 for analysis.

RESULTS AND DISCUSSION

The rate of biodegradation should be dependent on one of two factors: (1) transport of the carbon source to the soil microbes; (2) utilization of the carbon source by the microbes. Soil microbes exist within water films and pore space waters of the soil matrix. The carbon source must move from the vapor (gas) phase across the gas/liquid interface and through the liquid to the microbes. Diffusion is the primary driving force and is dependent upon the concentration gradient. Transport, or availability, will be the limiting step under conditions of lower concentrations because the concentration gradient (driving force) will be low. It would take longer to move the carbon source to the microbes than it would take the microbes to utilize it. High vapor phase concentrations will produce a large driving force for transport, thus utilization by soil microbes will be the limiting step.

Soil Types and Moisture Contents

Table 1 lists the individual characteristics of each soil examined in this study. The main physical differences between the soils were the grain size distributions and the permeabilities. Table 2 lists the final moisture contents of the soil columns.

lune, Eastman industrial grade ethylbenzene, and Aldrich 97% purity o-xylene. Chemical purity was confirmed with analysis by gas chromatography.

Soil Columns

Soil columns were constructed from 7.6 cm internal diameter beaded process pipe. The column length varied from 86.4 cm to 96.5 cm. The columns were filled with soil by lightly tamping the soil into the column as well water was pumped up through the bottom of the column. The well water was obtained from a local source near Ada, Oklahoma. This technique allowed settling of the soil without physically packing and destroying the natural soil aggregates. Once filled, the water was pumped out of the column and an air stream was introduced into the bottom of the column to establish a flow up through the column.

The soils examined in this study included Dougherty Sand and Durant Loam which are found locally around Ada, Oklahoma, and Rubicon Sand from Traverse City, Michigan. All soils were gathered from surface locations.

A hydrocarbon vapor stream was generated by purging air through vials containing the desired hydrocarbon and then

SOIL TYPE	MOIST BULK DENSITY (gm/cm³)	PERMEABILITY (in/hr)	SOIL REACTION pH	% ORGANIC MATTER	% PASSING SIEVE			
					no. 4 4.7 mm	no. 10 2.0 mm	no. 40 0.42 mm	no. 200 0.074 mm
DOUGHERTY SAND*		0.63–2	5.6–6.5	0.79	100	100	65–80	13–30
DURANT LOAM*		<0.6	5.6–6.5	0.75	100	100	95–100	55–85
RUBICON SAND**	1.35–1.55	6–20	4.5–6.0	0.5–1.0	95–100	75–100	35–70	0–15

Table 1 Soil Characteristics

*(reference 10)
**(reference 11)

Table 2 Soil Column Moisture Contents			
SOIL TYPE		PERCENT MOISTURE CONTENT (WET BASIS)	PERCENT OF SATURATION
DURANT LOAM	lower 28 cm	19.6	88
	upper 25 cm	11.4	51
DOUGHERTY SAND	lower 48 cm	10.4	46
	upper 25 cm	6.8	30
RUBICON SAND			
COLUMN F	lower 15 cm	17.7	saturated
	middle 25 cm	11.2	63
	upper 25 cm	9.4	53
COLUMN G	lower 15 cm	13.4	76
	middle 25 cm	9.5	54
	upper 25 cm	10.0	56

Inhibition due to excessive moisture was not directly addressed and was not observed in the experiments performed in this study. Additional differences between the soil columns were the length of the columns (50 to 75 cm) and the types of microbial populations present in each soil. Table 3 presents a summary of the percentage of each compound remaining in the effluent from the three soils examined under similar operating conditions. The percentage removal is the difference between 100% and the percent remaining.

Dougherty Sand showed a distinct preference for benzene (20.0–27.6% removal) and showed little utilization of o-xylene (5.0–11.0% removal). The Dougherty Sand soil column had the lowest percent water saturation values of the soil columns studied. Benzene was preferentially utilized because it was the simplest carbon source available or because the types of microorganisms present in the Dougherty Sand soil simply could not utilize the doubly methylated o-xylene. Subsequent microcosm experiments showed the upper sections of this soil column had reduced microbial activities. The short residence time in the bioactive portion of the column may have limited the overall removal ability of the column. Similarly, the Dougherty Sand soil column did not effectively remove toluene (8.3–10.1% removal). Again, possibly the presence of the methyl group inhibited the microbes from utilizing the toluene.

Alternatively, the Dougherty Sand did show potential for ethylbenzene utilization (12.9–23.1% removal). The types of microbes present in the Dougherty Sand seem to make a distinction between the ethyl-substituted ethylbenzene and the methyl-substituted toluene and o-xylene. The low relative moisture content of the Dougherty Sand soil column may have contributed to the limited utilization of the methyl-substituted hydrocarbons.

Durant Loam soil displayed equal removals of the four hydrocarbons. The Durant Loam soil column removed 11.4–17.8% of the benzene, 11.9–15.7% of the toluene, 13.5–15.9% of the ethylbenzene, and 11.8–15.4% of the o-xylene introduced into the column. The relative moisture content of the column was 51–88% of the saturation value. This moisture content was close to the optimum range of 50–70% of saturation capacity [9]. Adequate retention times within the optimum moisture portion of the column may have allowed equal utilization of the respective hydrocarbons. Moistures within this optimum range possibly allow microbial development which can utilize the available hydrocarbon sources equally.

Soil columns of Rubicon Sand also removed nearly equal percentages of each hydrocarbon. The columns removed 25.6–35.1% of the benzene, 28.0–37.4% of the toluene, 32.7–43.8% of the ethylbenze, and 27.8–39.8% of the o-xylene. The Rub-

Table 3 Hydrocarbon Removal by Different Soils				
COMPOUND	SOIL TYPE		INLET CONCENTRATION* μg/ml air	PERCENT REMAINING**
BENZENE	DOUGHERTY SAND		33.1	76.2 ± 3.8
	DURANT LOAM		31.2	85.4 ± 3.2
	RUBICON SAND	(F)	20.3	70.2 ± 4.2
		(G)	20.5	68.8 ± 3.9
TOLUENE	DOUGHERTY SAND		9.6	90.8 ± 0.9
	DURANT LOAM		8.7	86.2 ± 1.9
	RUBICON SAND	(F)	4.5	68.7 ± 3.3
		(G)	4.7	66.9 ± 4.3
ETHYLBENZENE	DOUGHERTY SAND		3.5	82.0 ± 5.1
	DURANT LOAM		3.4	85.3 ± 1.2
	RUBICON SAND	(F)	1.8	61.2 ± 5.0
		(G)	1.2	62.2 ± 5.1
O-XYLENE	DOUGHERTY SAND		2.4	92.0 ± 3.0
	DURANT LOAM		2.7	86.4 ± 1.8
	RUBICON SAND	(F)	0.9	68.2 ± 4.0
		(G)	0.9	66.2 ± 6.0

* average inlet concentration
** average of percent remaining data
40 ml/min air flow rate

FIGURE 2. Influence of concentration on benzene removal. Rubicon Sand soil column.
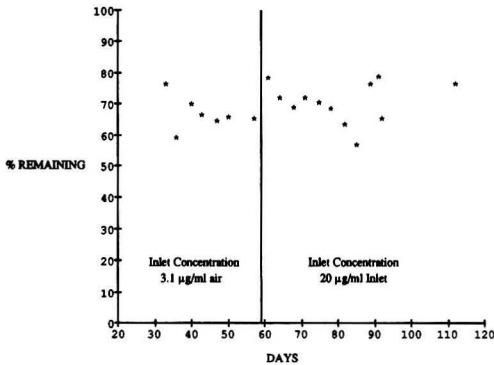
AIR FLOW RATE 40 ml/min

FIGURE 3. Influence of concentration on benzene removal. Dougherty Sand soil column.

AIR FLOW RATE 10 ml/min

icon Sand had the greatest moisture content throughout the soil column of the three soils examined. Moisture contents greater than 50% of saturation were present along the entire length of the column. Adequate moisture throughout the entire

column allowed ample residence time within the bioactive portion of the column so all hydrocarbons could be partially degraded. Adequate moistures possibly allow diverse development of microorganisms or stimulate the indigenous microbes to utilize whatever carbon source is available to them.

Table 4 Hydrocarbon Removal at Varying Inlet Concentrations

SOIL TYPE	FLOW RATE* ml air/min	COMPOUND	INLET CONCENTRATION* μg/ml air	PERCENT REMAINING**
RUBICON SAND COLUMN F	40	BENZENE	3.1	66.4 ± 4.9
			20.3	70.2 ± 4.2
		TOLUENE	1.1	64.8 ± 3.0
			4.5	68.7 ± 3.3
		ETHYLBENZENE	0.9	53.2 ± 4.4
			1.3	61.2 ± 5.0
		O-XYLENE	1.0	64.8 ± 5.6
			0.9	68.2 ± 4.0
RUBICON SAND COLUMN G	40	BENZENE	3.1	67.5 ± 5.1
			20.5	68.8 ± 3.9
		TOLUENE	1.5	57.6 ± 4.8
			4.7	66.9 ± 4.3
		ETHYLBENZENE	1.1	58.1 ± 2.4
			1.2	62.2 ± 5.1
		O-XYLENE	1.1	62.4 ± 3.4
			0.9	66.2 ± 6.0
DOUGHERTY SAND	10	BENZENE	35.2	69.1 ± 2.4
			4.1	4.2 ± 1.0
		TOLUENE	9.5	76.7 ± 2.2
			2.9	73.3 ± 4.7
		ETHYLBENZENE	3.9	72.2 ± 3.1
			4.0	72.8 ± 10.2
		O-XYLENE	2.6	82.2 ± 3.4
			4.9	Note 1
DURANT LOAM	10	BENZENE	35.6	69.9 ± 1.8
			3.9	8.5 ± 5.9
		TOLUENE	10.3	76.4 ± 1.9
			3.8	65.0 ± 9.4
		ETHYLBENZENE	3.6	73.1 ± 3.2
			3.7	73.5 ± 8.0
		O-XYLENE	2.6	77.2 ± 3.6
			4.5	Note 1

*average of flow rate and inlet concentration
** average of percent remaining data
Note 1: steady state removal conditions not established

Inlet Concentration

Adjusting the inlet hydrocarbon concentration while maintaining a constant inlet air flow rate allows examination of different loading rates at constant column residence times. Figures 2 and 3 are examples of hydrocarbon removals as they are influenced by the inlet concentration. Figure 2 shows the amount of benzene removal obtained with a Rubicon Sand column when the inlet air flow rate was 40 ml/min. The average initial benzene concentration was 3.1 μg/ml air for the first 57 days and the average percent removal was 28.7-38.5% and 27.4-37.6% for columns F and G, respectively. As noted earlier, the average percentage removal is equal to 100% minus the percentage remaining. The concentration was increased to approximately 20 μg/ml air and the average percent removal reduced slightly to 25.6-34.0% and 28.0-35.8% of the inlet benzene for columns F and G, respectively. If first-order kinetics are assumed and the column efficiency remains the same (constant ratio of microbial population to hydrocarbon utilization), then the percentage removal depends only on the residence time in the reactor. The observed percentage removal was approximately the same at both concentrations, thus indicating a removal which follows first order kinetics. Table 4 lists the removals obtained at each operating condition for each of the soils examined.

Toluene also shows first-order removal characteristics in the Rubicon Sand column F. The toluene percent removal was less in column G at the higher inlet concentration which may indicate a shift from first-order toward zero order removal rates. Alternatively, the increased availability of benzene may have inhibited toluene removal at the higher inlet concentration. The ethylbenzene and o-xylene concentrations were held approximately constant throughout the experiment. The accompanying percent removals of ethylbenzene and o-xylene were slightly less during the high hydrocarbon loading portion of the experiment. This may have been caused by the increased utilization of the more readily available benzene and toluene.

Figure 3 shows the benzene removal obtained in the Dougherty Sand soil column at an air flow rate of 10 ml/min; the effect of having a high initial hydrocarbon loading rate and then lowering the loading rate is illustrated. The average initial concentration of benzene was 35 μg/ml air and resulted in an average percent removal of 28.5-33.3%. The average inlet concentration was then reduced to 4 μg/ml air and a removal greater than 90% of the inlet benzene was observed for the first week. After the first week, the percent removal started decreasing (the percent remaining increased) and was decreasing toward 70% removal (30% remaining) when the experiment was halted. A constant biomass to hydrocarbon loading ratio is expected in biological systems which are at equilibrium. The biomass will change in response to a change in the hydrocarbon loading rate. The decreasing percent removal reflected a decreasing biomass in response to the reduction of the hydrocarbon loading rate. Allowed to continue, the percent removal would probably have stabilized at about 30% if first-order kinetics are controlling.

Toluene removal in the Dougherty Sand column increased slightly as the inlet concentration which was started at a higher concentration was reduced to a lower concentration. The slight increase is probably the result of the temporary increase in the biomass to hydrocarbon ratio which accompanied the reduction in the hydrocarbon loading rate. Toluene removal did not display the decreasing removal efficiency over time which was characteristic of the benzene removal. The nearly complete removal of benzene at the lower concentration may have prompted additional toluene utilization as the microbe population readjusted to the new hydrocarbon loading rate.

The ethylbenzene inlet concentration was held constant throughout the experiment with the Dougherty Sand soil column. The increased microbial activity which produced large increases in benzene removal at the lower benzene concentra-

tion did not affect the ethylbenzene removal. The o-xylene inlet concentration was unintentionally increased when the hydrocarbon loading rate was decreased. O-xylene sorption/desorption was not at steady state at the conclusion of this experiment, and no trends could be established.

Durant Loam was also used to study the effects of decreasing the inlet concentrations. The inlet air flow rate was 10 ml/min. The average benzene concentration began at 35.6 g/ml air and was later decreased to 3.9 μg/ml air. Corresponding removal rates were 28.3-31.9% and 85.6-97.4%, respectively. As with the Dougherty sand discussed previously, a decreasing biomass accompanied the reduction of the hydrocarbon loading rate. The reduction of the biomass was evidenced by decreasing removals over time. If first order kinetics are assumed, the removal should stabilize at the initial level of about 30%. The study was terminated before the removal became stable.

The initial inlet toluene concentration in the Durant Loam column averaged 10.3 μg/ml air and removal ranged from 21.7-25.5%. The average inlet concentration was then reduced to 3.8 μg/ml air which resulted in a removal of 25.6-44.4% of the inlet toluene. The increased percent removal was probably caused by the increased microbial activity temporarily present after the reduction in the hydrocarbon loading rate.

The ethylbenzene inlet concentration was held constant in the Durant Loam column as the hydrocarbon loading rate was changed from high to low. Ethylbenzene inlet concentrations averaged 3.6 for the initial phase and 3.7 μg/ml air during the reduced hydrocarbon loading phase. Respective removals of 23.7-30.1% and 18.5-34.5% were observed. The increased biomass activity initially present when the hydrocarbon loading was reduced did not affect the ethylbenzene removals. Ethylbenzene was a small percentage of the initial hydrocarbon stream. The microbial community which acclimated to the original feed stream may not have been able to effectively utilize additional ethylbenzene as the benzene source was depleted.

The initial o-xylene inlet concentration averaged 2.6 μg/ml air and the Durant Loam soil column removed 19.2-26.4% of the inlet o-xylene. The o-xylene inlet concentration increased as conditions were changed from high hydrocarbon loading to low. This produced an unsteady removal condition for the o-xylene which did not reach equilibrium before termination of the experiment and no trends could be developed.

In general, when the inlet concentrations of the BTEX were increased the percent removal remained approximately the same or decreased only slightly. This indicates that the overall removal process follows first-order kinetics. When the inlet concentrations were decreased from a higher level, the relative percent removal increased due to the initially inflated biomass to hydrocarbon ratio. The greatest change was for benzene. The higher level of removal was only temporary, however. As the biomass to hydrocarbon ratio adjusted toward the initial value, the percent removals approached their initial values. Percent removals which are independent of loading rate are characteristic of first-order removal kinetics.

Inlet Flow Rate

Residence time within a soil column is determined by the flow rate of the inlet air stream, the length of the soil column, and the open pore volume. Reducing the air flow rate by 50% will theoretically double the residence time within the column but, at the same time, will cut the hydrocarbon loading rate in half. The biomass within the soil column will in turn adjust to the new loading rate and, as shown in the previous section, would produce the same percent removal if the residence time was unchanged and first-order biodegradation kinetics were controlling the removal process. Since the residence time increases with reductions in the air flow rate, increases in observed percentage removals may be expected from the soil
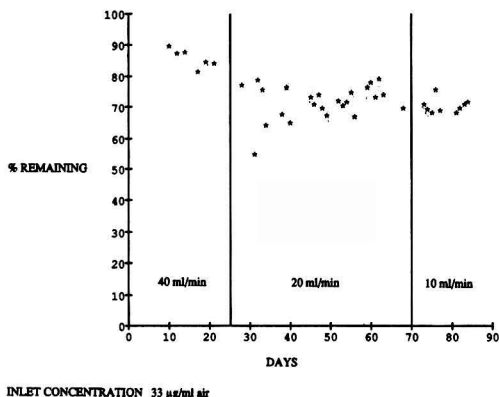
INLET CONCENTRATION 33 µg/ml air

FIGURE 4. Effect of flow rate on benzene removal. Durant Loam soil column.

the minimum concentration predicted by the transport limitations, increases in retention time would produce diminishing increases in percentage removals.

The Durant Loam soil column exhibited BTEX removals characteristic of first-order removal reactions as the inlet air flow rate was reduced to double the reaction time. Further reduction of the inlet air flow rate produced little improvement in the percentage removals, thus indicating that transport limitations were restricting the removal process. Figure 4 shows the removal of benzene in the Durant Loam soil column at an inlet concentration of approximately 30 µg/ml air. The average amount of removal increased from 15% to 29% to 30% for air flow rates of 40, 20, and 10 ml/min, respectively. As expected, longer retention times produced greater removals. Reducing the inlet air flow from 40 ml/min to 20 ml/min resulted in an increased removal (from 15% up to 29% removed) consistent with first-order removal kinetics for a doubling of the residence time. Further reduction of the air flow rate from 20 ml/min to 10 ml/min did not appreciably increase the removal efficiency. Possibly the overall removal reaction was changing from removal rate limited to transport limited. As such, increasing the residence time will produce negligible increases in the percentage removed for conditions in which the outlet concentration approaches the transport limiting minimum concentration. The effect of inlet air flow rate was similar for the other compounds tested, toluene, ethylbenzene, o-xylene. Table 5 lists a summary of the results from changing inlet air flow rates.

Hydrocarbon removals in the Dougherty Sand soil column increased with increased retention times, but the removal processes seemed to be limited more by transport than by biodegradation rates. Benzene inlet concentrations ranged from approximately 32 to 35 µg/ml air over the course of the air flow rate experiment. The benzene removals increased slightly

columns. Increases in removal will follow first-order removal kinetics until the removal process becomes transport limited. Removals then become a function of the biodegradation rate and the rate of transport. During periods of low loading rates the concentration gradient between the bulk fluid and the reaction site (which drives the transport process) would be small and transport would be reduced. As retention times are increased within a given column, the outlet hydrocarbon concentration should asymptotically approach a minimum concentration which is limited by the transport of the reactant to the reaction site. As the outlet concentration approaches

Table 5 Hydrocarbon Removal at Varying Flow Rates				
SOIL TYPE	COMPOUND	FLOW RATE* ml air/min	INLET CONCENTRATION* µg/ml air	PERCENT REMAINING**
DURANT LOAM	BENZENE	40	31.2	85.4 ± 3.2
		20	33.0	71.3 ± 2.4
		10	35.6	69.9 ± 1.8
	TOLUENE	40	8.7	86.2 ± 1.9
		20	8.9	79.4 ± 2.1
		10	10.3	76.4 ± 1.9
	ETHYLBENZENE	40	3.4	85.3 ± 1.2
		20	3.3	74.3 ± 2.7
		10	3.6	73.1 ± 3.2
	O-XYLENE	40	2.7	86.4 ± 1.8
		20	2.5	72.7 ± 2.6
		10	2.6	77.2 ± 3.6
DOUGHERTY SAND	BENZENE	40	33.1	76.2 ± 3.8
		20	31.9	75.4 ± 2.7
		10	35.2	69.1 ± 2.4
	TOLUENE	40	9.6	90.8 ± 0.9
		20	8.7	79.4 ± 2.5
		10	9.5	76.7 ± 2.2
	ETHYLBENZENE	40	3.5	82.0 ± 5.1
		20	3.6	72.0 ± 2.6
		10	3.9	72.2 ± 3.1
	O-XYLENE	40	2.4	92.0 ± 3.0
		20	2.5	79.7 ± 2.2
		10	2.6	82.2 ± 3.4

*average flow rate and inlet concentration
**average of percent remaining data

INLET CONCENTRATION 9 μg/ml air

FIGURE 5. Effect of flow rate on toluene removal. Dougherty Sand soil column.

from 24% to 25% to 31% for air flow rates of 40, 20, and 10 ml/min, respectively. The benzene removal did not increase significantly between the 40 and 20 ml/min inlet air flow rates, possibly due to increased utilization of alternative hydrocarbons. Utilization of toluene, ethylbenzene, and o-xylene increased by 12%, 10%, and 12%, respectively, when the inlet air flow rate was changed from 40 to 20 ml/min. An additional reduction in the air flow rate from 20 to 10 ml/min produced an additional 6% removal of benzene. The overall removal process was possibly controlled by a combined effect of biodegradation kinetics and transport limitations.

Figure 5 depicts the removal of toluene in the Dougherty sand soil column with an average inlet toluene concentration of 9.3 μg/ml air. The reduction of the air flow rate from 40 to 20 ml/min produced an increase in removal from 9% to 21%. This increase in removal corresponds to a first-order biodegradation rate controlling the removal process. A further reduction in the inlet air flow rate from 20 to 10 ml/min produced only a slight increase in the percentage toluene removal (to 23%). Transport limitations would restrict increases in the percentage removal and are probably controlling the removal process at this point. The ethylbenzene and o-xylene removals also indicated that a first-order biodegradation rate was initially controlling the process. Further reductions in the inlet air flow rate from 20 to 10 ml/min produced limited increases in removals, thus indicating that the removal process is transport limited at the lower inlet air flow rate.

In general, decreased air flow rates resulted in increased percentage removals for BTEX. Decreasing the air flow rate from 40 ml/min to 20 ml/min increased removals; this indicated the removal process was controlled by first-order biodegradation kinetics. Further reductions in the air flow rate resulted in diminished increases in the removals; this indicated that the removal process was becoming transport-limited. Therefore, reduction in inlet air flow rates may not always produce expected increases in the percent removal of BTEX. An alternative to decreasing the inlet air flow rate (and reducing the biomass) would be to keep the air flow rate constant and simply double the length of the column. This would allow greater percentage removals up to the point that transport becomes the limiting factor in the removal process. Further experiments need to be conducted to determine the minimum effluent concentrations caused by transport limitations. Further work also needs to examine grain size distribution, organic carbon content, and other design factors which may influence the minimum effluent concentration.

SUMMARY AND CONCLUSIONS

Soil columns were utilized to examine the hydrocarbon (BTEX) vapor degradation potential of three soil types. The three soils were Rubicon Sand from Traverse City, Michigan, Durrant Loam from Ada, Oklahoma, and Dougherty Sand from Stratford, Oklahoma. Hydrocarbon removal was observed with each soil tested. Soil which had adequate available moisture (>50% saturation throughout the column) showed equal utilization of the BTEX compounds. Soil which had moisture contents less than 50% of saturation displayed preferential utilization of benzene followed by ethylbenzene. The percentage removals of the BTEX compounds were independent of the inlet concentrations used in this study (from about 1 to 35 μg/ml air), thus indicating that the biodegradation rates were first order. Decreasing the inlet air flow rates (from 40 to 10 ml/min) at constant inlet concentrations demonstrated that the removal process was controlled initially by a first order-type biodegradation rate, but then became limited by transport properties at lower inlet air flow rates.

The results of this study indicate that microbe populations of various soil types are capable of biodegrading BTEX vapor streams. A soil bioreactor should be effective at treating waste gas streams of BTEX compounds if adequate contact times are utilized. Increasing the depth of the soil bioreactor should produce greater removal efficiencies unless the removal process has a lower concentration limit. Further studies will be required to determine if the transport limitations encountered at the low inlet air flow rates will limit the removal efficiency of field scale bioreactors.

ACKNOWLEDGEMENTS

LITERATURE CITED

1. U.S. EPA, EPA/600/2-87/008 (Jan. 1987).
2. Marrin, D. L. and H. B. Kerfoot, *Environ. Sci. and Tech.*, 22, pp. 740–745 (July 1988).
3. Canter, L. W. and R. C. Knox, "Ground Water Pollution Control," Lewis Publishers, Chelsea, MI (1986).
4. Zimmermann, R. E. and V. M. Brizgys, "Remediation of Subsurface Contamination From Volatile Organic Compounds Using Soil Gas Extraction Techniques," Proceedings of the Sixth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring, pp. 580–591 (May 1986).
5. Bohn, H. L., "Soil for Management of Organic Wastes and Waste Waters," pp. 607–617, Soil Science Society of America, Madison, WI (1977).
6. Hoeks, J., *Soil Science*, 113, pp. 46–54 (1972).
7. Kampbell, D., et al., *Air Poll. Con. Ass. J.*, 37, pp. 1236–1240 (Oct. 1987).
8. Prokop, W. H., and H. L. Bohn, *Air Poll. Con. Ass. J.*, 35, pp. 1332–1338 (Dec. 1985).
9. Dibble, J. T., and R. Bartha, *Appl. and Environ. Micro.*, 37, pp. 729–739 (Apr. 1979).
10. U.S. Department of Agriculture/Soil Conservation Service, "Soil Survey of Pontotoc County, OK" (April 1973).
11. U.S. Department of Agriculture/Soil Conservation Service, "Soil Interpretation Record, Rubicon Series, Grand Traverse Country, MI" (July 1986).

Implications of the Clean Air Act Acid Rain Title on Industrial Boilers

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This paper discusses the impacts of the 1990 Clean Air Act Amendments related to acid rain controls, as they apply to industrial boilers. Emphasis is placed on explaining the Title IV provisions of the Amendments that permit "nonutility" sources to participate in the SO_2 allowance system. The allowance system, as it pertains to industrial boiler operators, is described, and the opportunities for operators to trade and/or sell SO_2 emission credits is discussed.

The paper also reviews flue gas desulfurization system technologies available for industrial boiler operators who may choose to participate in the system. Furnace sorbent injection, advanced silicate process, lime spray drying, dry sorbent injection, and limestone scrubbing are described, including statements of their SO_2 removing capability, commercial status, and costs. Capital costs, levelized costs and cost-effectiveness are presented for these technologies.

INTRODUCTION

One and a half years of debate and negotiation have produced the acid rain title (Title IV) of the 1990 Clean Air Act Amendments (CAAA), approved by the 101st Congress on October 27 and signed into law by the President on November 15, 1990. Title IV of the CAAA establishes a system of allowances for SO_2 and NO_x emissions for utility units, and the measure intended to reduce acid gas pollutant emissions from these units. For control of SO_2 emissions, the legislation provides a two-phase program. In Phase I, the legislation imposes an annual emission limit of 2.5 lb/MMBtu on 110 utility plants. In Phase II, a more stringent annual emission of 1.2 lb/MMBtu would be applied to utility units in operation before enactment that produce more than 25 MW.

The first part of this paper explains the Title IV provisions of the CAAA that permit "nonutility" sources to participate in the SO_2 allowance system. The allowance system, as it pertains to industrial boiler operators, is described, as well as opportunities for those operators to trade or sell SO_2 emission credits. The latter part of this paper reviews flue gas desulfurization (FGD) technologies available to nonutility operators, including descriptions of the processes and a discussion of their costs.

OPTIONS FOR NONUTILITY UNITS

The legislation provides a market-based approach to acid deposition control rather than mandating "Command and Control" regulations. Each regulated source would obtain a certain number of SO_2 emission allowances (one allowance is equal to one ton of SO_2) each year, based on the applicable emission limit. An allowance could be used in the same year it was acquired, saved for future years, shared with other regulated units, or sold to other sources. Thus, allowance holders could buy and sell allowances on the open market, encouraging reduction of emissions in a cost-effective manner.

Although allowances will be allocated to existing utility units, any unit that is not, nor will become, an affected unit under Title IV may elect into the allowance system. Some of the units that emit SO_2 but are not affected by Phase I or II requirements of the CAAA include: existing small utility units (25 MW or less), industrial boilers, and simple-cycle combustion turbines. Pursuant to Section 410 of the CAAA, owners or operators of industrial and process sources that emit SO_2 but are covered under Title IV may elect to designate those sources as affected units. These sources would then have the opportunity to receive allowances in an amount equal to their actual or allowable 1985 emissions, whichever is the lowest, reduce their emissions,
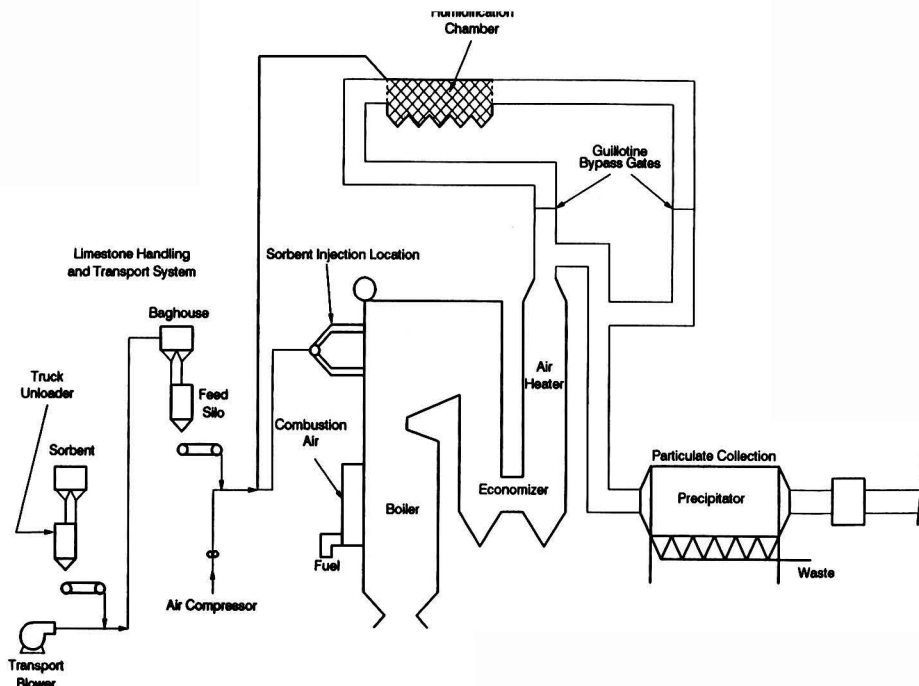
FIGURE 1. Furnace sorbent injection.

and transfer or sell their allowances. To qualify, a source must submit an election to opt into the program, a permit application, and a proposed compliance plan that meets the requirements of Title IV to the Environmental Protection Agency (EPA). Sources will also need to demonstrate that they have installed and are operating qualified emissions monitoring equipment. Opt-in sources are restricted from transferring or banking allowances produced as a result of reduced utilization or shutdown. Allowances are transferable when a facility replaces one thermal energy unit with another or other units subject to the requirements of the CAAA. The EPA must promulgate regulations concerning this program by May 15, 1992.

Emission limitations for industrial sources that opt into this program will be calculated by multiplying a unit's baseline heat input (based on emissions in 1985, 1986, or 1987, or an alternative baseline established by EPA) by the lesser of the unit's 1985 actual or allowable rate in lb SO_2/MMBtu. If the unit did not operate in 1985, the emission allowances for that unit will be determined by EPA.

Much is left undefined in the CAAA, including the dollar value of the allowances, which could be worth as much as $2,000 per ton. For example, the penalty for emitting SO_2 in excess of the allowances that an operator holds for a given year is $2,000 per ton of excess emissions. However, the operator of a unit can purchase the extra allowances needed to offset the excess emissions on the open market, directly from EPA at a fixed price, or at annual auctions to be held by EPA.

OPT-IN REQUIREMENTS

Nonutility units opting into the program should fit into one of the following three categories:
- units that emit SO_2 but are not affected units under Phase I or II or new unit provisions;
- qualified process sources that emit SO_2, pursuant to section 410(d) of the CAAA; and

- small diesel refineries, pursuant to section 410(h
The following guidelines apply to units opting into t gram:
- opt-in units will receive allowances.
- opt-in units are subject to the requirements outl the CAAA under the following sections:
  - 403—allowances,
  - 408—permits,
  - 411—excess emissions,
  - 412—emissions monitoring, reporting, and repor ing,
  - 413—general compliance with the CAAA, and
  - 414—enforcement.
- opt-in are subject to limitations regarding the allc and use of allowances by election sources, pursi section 410(f).
- opt-in units are subject to limitations regarding diesel refineries, as specified under section 211(allowances per refinery under section 410(h).

Pursuant to section 410(a) of the CAAA, the permit cation and compliance plan must include the followin;
- demonstration that the unit or source is one of th types of eligible sources;
- actual and allowable 1985 emission rates;
- operating data, fuel consumption, and other re emission baseline data;
- demonstration of operable continuous monitoring ment;
- compliance with the requirements for process sou section 410(d) of the CAAA;
- information regarding utilization [(section 410(f); ample, historical thermal energy generation)];
- demonstration of historical compliance with ot quirements of the CAAA [(section 410(f))]; and
- other data as may be required by future regulati
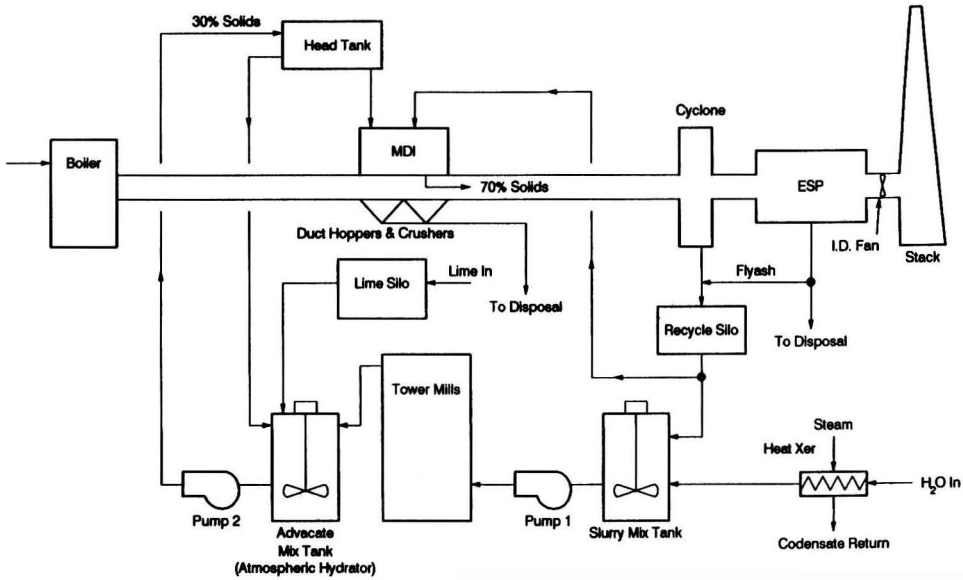
Case 1: Furnace Limestone Injection
Case 2: Lime Addition

FIGURE 2. Advacate FGD system.

AVAILABLE SO$_2$ REMOVAL TECHNOLOGIES

To comply with the SO$_2$ emission requirements of the legislation, opt-in sources can choose one or a combination of the following:

- switch to fuel with a lower sulfur content;
- implement emission control measures; or
- reduce utilization of the affected unit(s) if the thermal energy is being replaced with other unit(s) subject to the requirements of the CAAA.
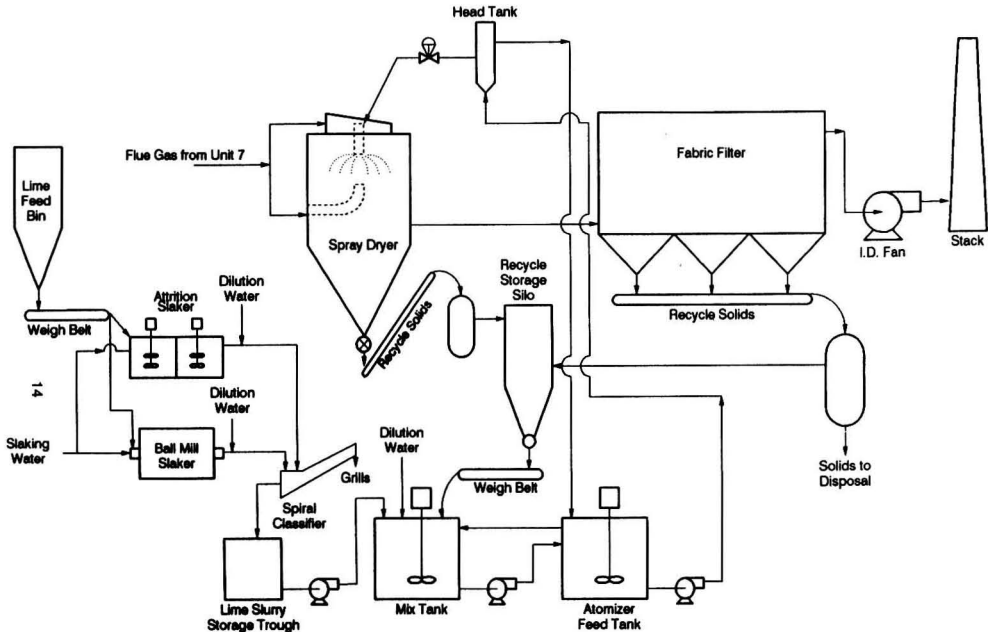
FIGURE 3. Lime spray dryer process flow diagram.

EMISSION CONTROL MEASURES

A number of high- and low-efficiency FGD technologies are available for SO$_2$ removal. Some of the dry and wet FGD technologies considered in this study are [1]:
- furnace sorbent injection (FSI);
- advanced silicate (ADVACATE);
- lime spray drying (LSD);
- dry sorbent injection (DSI) using Nahcolite; and
- lime/limestone wet FGD (L/LS FGD).

In the following sections, brief process descriptions of each of these technologies are presented, along with their commercial status and expected removal efficiencies. Comparable technologies are available, but are not considered here. Sodium hydroxide wet scrubbing is frequently used to remove SO$_2$ from industrial units. However, costs for sodium wet scrubbing process was not available; therefore, this technology is not discussed in this paper.

Furnace Sorbent Injection

The FSI process (also referred to as lime injection multistage burner—LIMB) reduces SO$_2$ emissions by injecting powdered calcitic hydrate into the upper furnace of a coal-fired boiler (Figure 1). Sorbent decomposes at high temperature to form calcium oxide, which reacts with SO$_2$ to form calcium sulfate (CaSO$_4$). The extent of SO$_2$ removal that can be achieved depends on the flue gas composition, temperature, and quench rate at the point of sorbent injection; sorbent composition and surface area; the calcium-to-sulfur ratio (Ca/S); and the degree of mixing between the sorbent and the SO$_2$ in the flue gas. The resulting CaSO$_4$ and unreacted sorbent are collected with the flyash in a baghouse or electrostatic precipitator (ESP).

Collected sorbent and flyash can be either recycled to the furnace to increase sorbent utilization or discharged to solid waste disposal facilities. Presently, three commercial-scale utility projects in the United States are demonstrating FSI on eastern bituminous coal-fired boilers. FSI removal efficiency typically ranges from 40 to 70 percent.

Advanced Silicate

The ADVACATE process is a throwaway system in which damp, highly reactive calcium silicate hydrates are injected into the flue gas following the air heater to absorb SO$_2$ and form a calcium sulfite/sulfate waste material (Figure 2). The sorbent is flash-dried in the duct and then collected in a downstream particulate control device.

In the ADVACATE process, lime is added to a slurry mixed tank where it reacts with the silicon dioxide present in the flyash to form calcium silicates. The product is ground in tower mills to form high-surface-area particulates. The calcium hydroxides and silicates are mixed with more flyash to about 60 to 70 percent solids content. The prepared sorbent is then injected into the duct upstream of the particulate control system. Sulfur dioxide in the flue gas is absorbed on the surface of the calcium silicate particles and reacts to form calcium sulfite/sulfate. These products are collected in a particulate control device and either recycled or sent to disposal.

The ADVACATE process is an outgrowth of LSD and FSI research sponsored by EPA and is being developed as a cost-effective alternative to conventional limestone and LSD technologies. The ADVACATE system is not yet commercially available. The Tennessee Valley Authority plans to install a 10-MW demonstration unit in 1991 or 1992. The predicted removal efficiency for the ADVACATE system is around 90 percent.
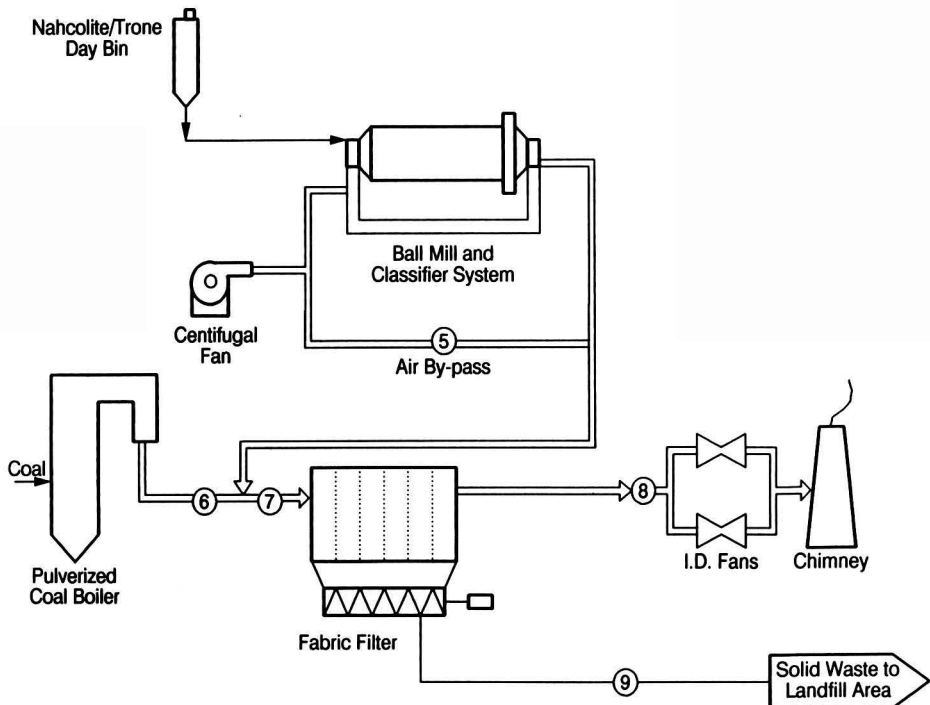
FIGURE 4. Dry sorbent injection.
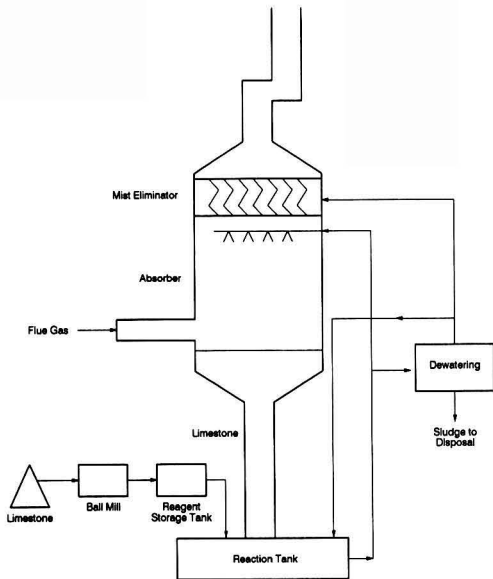
FIGURE 5. Limestone FGD system.

Lime Spray Drying

Lime spray drying is an established post-combustion FGD technology for coal-fired boilers. The removal efficiency for LSD ranges from 80 to 90 percent. In an LSD system, lime slurry is atomized inside a spray dryer chamber, where heat from the flue gas causes evaporation of the water in the atomized slurry (Figure 3). The SO_2 in the flue gas is absorbed

into the alkaline slurry, reacting with the lime to produce a mixture of calcium salts. Some of the solids are collected at the bottom of the spray dryer, while the remaining solids leave with the flue gas. The flue gas enters the particulate collection device, where additional SO_2 removal occurs. LSD removal efficiency typically ranges from 70–90 percent.

Dry Sorbent Injection Using Nahcolite

Dry sorbent injection is a post-combustion FGD technology. In DSI, a dry alkaline material (for example, Nahcolite) is pneumatically injected into the duct; an ESP or fabric filter downstream provides particulate collection (Figure 4). The removal efficiency of the process is a function of the amount of sorbent used. Typical removal efficiencies range from 50 to 80 percent. The DSI technology using Nahcolite is commercially available.

LIME/LIMESTONE WET FGD

Lime/limestone wet scrubbing is the most common post-combustion control technique currently applied to utility boilers. The expected removal efficiency of a wet system is about 90 to 95 percent. Today, more than 150 coal-fired boilers in the United States with a total generating capacity of 72 GW operate with FGD.

Most of the L/LS FGD systems operating in the United States use calcium-based reagents. Wet FGD systems use an alkaline sorbent in a water solution or slurry to absorb SO_2 from the combustion flue gas (Figure 5). Wastes are commonly disposed of in landfills or in holding ponds.

COST ESTIMATES FOR FGD TECHNOLOGIES

The Integrated Air Pollution Control System (IAPCS) cost model was used to develop FGD costs [2]. Table 1 presents capital cost, levelized cost, and cost-per-ton of SO_2 removed for the technologies described above for an industrial unit rated at 600 MMBtu/hr unit (65 equivalent Mwe operating with a capacity factor of 65 percent). Costs are presented for both

Table 1 SO₂ Control Cost Estimates For An Industrial Boiler Equivalent To 60 MWe and 65% Capacity Factor (November 1990 $)

	FSI		ADVACATE		LSD		DSI		LS-FGD	
	Hi S%	Low S%	Hi S%	Low S%	Hi S%	Low S%	Hi S%	Low S%	Hi S%	Low S%
SO₂ Removal	50	50	90	90	90	90	70	70	90	90
Capital Cost										
$/KW	95	75	235	210	560	340	200	105	445	340
Levelized Cost										
Mills/KWh										
Current $	17.6	8.7	21.9	15.1	37-.8	21.6	43-.7	11.8	28.8	20.6
Constant $	10.2	5.0	12.7	8.7	21-.8	12.5	25-.3	6.8	16.6	11.9
Cost Effectiveness										
$/Ton SO₂ Removed										
Current $	900	2,440	620	2,350	1,045	3,290	1,590	2,350	815	3,210
Constant $	520	1,410	360	1,360	600	1,900	920	1,360	470	1,860

FSI—Furnace Sorbent Injection (also referred to as LIMB)
ADVACATE—Advance Silicate Process (using limestone)
LSD—Lime Spray Drying (using lime)
DSI—Dry Sorbent Injection (using nahcolite)
LS-FGD—Limestone Flue Gas Desulfurization

Hi S%—High Sulfur Coal, Illinois No. 6 (4.0% sulfur)
Low S%—Low Sulfur Coal, West Virginia (0.9% sulfur)

Current $—Cost in Current November 1990 $

Constant $—Cost in Constant November 1990 $

Table 2 Summary of Economic Assumptions

Current Carrying Charges	0.1754
Constant Carrying Charges	0.105
Current O&M Charges	1.75
Constant O&M Charges	1.00
Nahcolite	210.0 $/ton
Limestone	16.0 $/ton
Lime	60.0 $/ton
Labor Rate	21.0 $/hr
Waste Disposal, Dry	8.5 $/ton
Waste Disposal, Wet	9.8 $/ton
Water	0.6 $/1,000 gal
Electricity	52.8 mills/KWH
Inflation Rate	6.0 percent

Carrying Charges: The revenue needed to support an investment.

O&M: Operating and Maintenance.

Current Dollar Analysis: An analysis that includes the effect of inflation and real escalation.

Constant Dollar Analysis: An analysis made without including the effect of inflation.

high-sulfur (4.0 percent Illinois No. 6 coal) and low-sulfur cases (0.9 percent West Virginia coal). Table 2 summarizes the economic assumptions used in this study. Costs are in 1990 constant and current dollars. For constant dollars, a zero inflation rate was used.

As shown in Table 1, FSI has the lowest capital cost estimates ($75–$95/Kw), while ADVACATE has the lowest cost per ton of SO_2 removed ($360–$1,360/ton). The more capital-intensive technologies with high SO_2 removal tend to be cost-effective when they burn high-sulfur coal and have high capacity factors. Figures 6 through 8 graphically present the capital costs, levelized costs, and cost-per-ton of SO_2 removed for high- and low-sulfur coals in constant dollars.
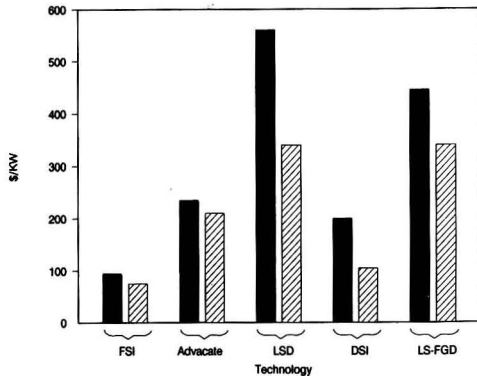
Based on a study conducted for EPA on 200 coal-burning utility plants in the eastern United States [3], cost-per-ton of SO_2 removed using L/LS FGD ranged from $200 to $8,000/ton (Figure 9). Of 449 units considered applicable for L/LS FGD in the study, the cost-per-ton of SO_2 removed for 75 percent of the units was higher than $500/ton. All these units are utility units and, as such, must meet CAAA emission limits. The 200-plant database was also used to review a combination of different FGD techniques to estimate the most cost-effective "average cost per ton." To remove 8 million tons of SO_2 annually, it was estimated that a combination of coal switching and blending ($15 per ton fuel price differential), FSI, and L/LS FGD technologies would result in a weighted average of $480/ton. To remove 10 million tons of SO_2 from 1980 emission levels (as called for by the CAAA), the cost would be well above $500/ton (constant dollars). Industrial units not affected by the CAAA could opt into the program if they are more cost-effective in removing SO_2 than utility units affected by the regulations.

For retrofit application of these technologies, different factors affect control cost and performance estimates. In most cases, site access and congestion, flue gas ducting distances, and particulate control addition/modification (if required) are major cost factors. The final cost analysis must take into account that the technologies evaluated in this study are at various

FIGURE 6. Capital cost.
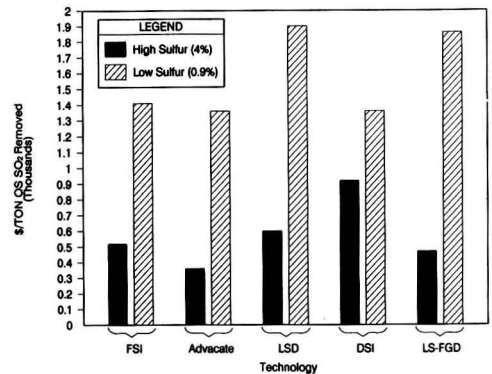
FIGURE 8. Cost effectiveness.
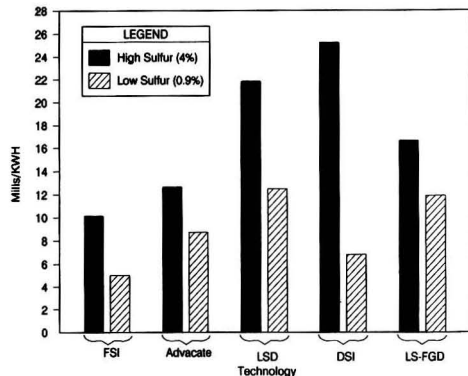
FIGURE 7. Levelized cost.
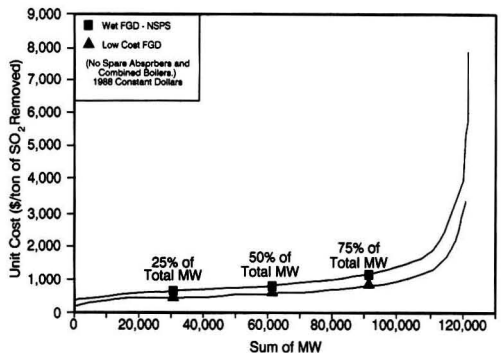
FIGURE 9. Summary of cost per ton of SO_2 removed results for lime/limestone flue gas desulfurization.

stages of commercial development. There is a higher degree of uncertainty regarding the costs and performance for those technologies that do not have extensive commercial application.

CONCLUSIONS

Section 410 of the CAAA was intended to serve both the market and the environment by providing additional allowances to reduce compliance costs for affected utilities, as well as encourage early voluntary reductions.

In cases where it would be prohibitively expensive to scrub utility units or where electrical growth is needed but no allowances are left in the system, nonutility units can opt into the CAAA program and participate in the emission allowance market. If a nonutility unit can scrub SO_2 for less than $1000/ton, opting into the program should be *considered*. A preliminary feasibility study should be performed on nonutility units to estimate the cost-effectiveness. However, the advantages of opting into the allowance system are difficult to fully evaluate until the final decision concerning the regulations are announced by EPA.

LITERATURE CITED

1. White, D., and M. Maibodi, "Control Technologies for Reducing Emission of SO_2 and NO_x from Existing Coal-Fired Utility Boilers," EPA/600/S7-90/018, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711 (January 1991).
2. Maibodi, M., A. L. Blackard, and R. J. Page, "Integrated Air Pollution Control System, Version 4.0, Volume 2: Technical Documentation Manual," EPA-600/7-900-022b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711 (December 1990).
3. Emmel, T. E., and M. Maibodi, "Retrofit Costs for SO_2 and NO_x Control Options at 200 Coal-Fired Plants," EPA-600/7-90-021a, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711 (November 1990).

NO$_x$ Reduction by the Econ-Nox™ SCR Process

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SCR systems are used extensively in Japan and West Germany to eliminate 80–90% NO$_x$ emissions from utility boilers and industrial furnace stacks. Costs have been lowered considerably over the past ten years. Further reduced costs and stringent regulations on NO$_x$ emission make this simple system attractive for refinery and industrial process heaters, boilers, and gas turbines.

The Econ-Nox™ process uses a fluidized catalyst bed to accomplish selective total reduction of oxides of nitrogen to elemental nitrogen using ammonia as a reactant. The process can be designed for operating temperatures between 550°F and 750°F and for a wide range of operating variables.

The process brings together some old technology on selective reduction chemistry, relatively new fluidized bed oxidation techniques and a non-precious metal Econ-Acat™ catalyst which permits operation over a broader temperature range than has been practical in the past.

This paper reports some of the distinctions made between this reactor configuration and the historical thermal and catalytic systems used for this type of process.

INTRODUCTION

Nitric oxide contributes importantly to air pollution. In the atmosphere, it oxidizes slowly to nitrogen dioxide and various nitrates which tinge smog characteristically brown. Nitrogen dioxide, as part of the photochemical reaction that occurs with various hydrocarbons in the atmosphere, also contributes to the formation of aldehydes, ketones and organic nitrates. In the presence of light and oxygen, the dioxide forms ozone and nitric oxide—and so the cycle continues.

A rise in ozone concentration normally follows an increase of oxides of nitrogen in the atmosphere, such as occurs during periods of atmospheric inversion. Ozone itself not only irritates eyes and lungs, it also forms complex organic compounds, such as aldehydes and peroxyacetyl nitrate, which also contribute to eye and lung irritation.

Nitrogen dioxide, itself an irritant, also forms nitric acid in air with water vapor and rain, damaging materials of construction, vegetation and lung tissue.

Leaching of metals, such as aluminum, from soils by acid rain has raised concerns about aquatic food chain health effects. The ozone produced also cause adverse environmental effects such as crop and forest damage and visibility impairment.

NO$_x$ contributes to nitrification of rain which can "over-fertilize" the soil, leaving foliage more vulnerable to damage from cold, insects, and disease. This nitrification may disturb both land and water ecological systems if buffering by calcium, magnesium and potassium is insufficient.

In addition, NO$_x$ emissions lead to the formation of nitrous oxide (N$_2$O) which migrates to the upper atmosphere where it is apparently very stable, remaining for decades. In the Arctic and Antarctica ozone depletion areas nitrous oxide is used to calculate the expected amount of ozone at the higher altitudes where so-called Type I polar stratospheric clouds, mostly nitric acid trihydrate, form at about −77°C.

Nitrous oxide has been reported as inert relative to upper ozone depletion but these nitric acid trihydrate clouds provide a surface on which forms of chlorine that are relatively inert toward ozone are converted to destructive forms. In the polar spring, the active chlorine species begin to destroy ozone photochemically. N$_2$O concentrations in the atmosphere have reportedly been increasing by 0.2 to 0.4 percent each year over the past decade.

Utilities Have Options in Acid Rain Control

The TVA has acknowledged that NO_x is probably causing the more serious problems stemming from the increasing SO_x/NO_x releases from industrial furnaces.

The TVA expressed concern about the greater emphasis on SO_x removal than NO_x removal. They are worried that TVA will be subjected to the same fate as German utilities. They will make the required SO_2 reductions and then Congress will determine that NO_x is a worse pollutant than SO_x and more stringent NO_x control measures will be then implemented. The TVA points to the interim findings of the National Acid Precipitation Assessment Program supporting the argument that SO_2 emissions are less damaging than originally thought.

SCR Availability Up, Costs Down

A recent industry "white paper" stated, in part, "SCR systems are used extensively in West Germany and Japan to eliminate 80-90% of NO_x emissions from utility boilers, compared to the 40-50% removal efficiency of other NO_x control technologies" [1].

"The experience in Japan and Europe demonstrates that SCR works well when retrofitted on utility boilers. It is available for use on both medium and high sulfur coals. The South Coast Air Quality Management District (California) concluded that "SCR units are available at reasonable costs for retrofit with a demonstrated history of NO_x reduction ... and can be installed on a turn-key basis in approximately one year."

"Numerous authorities with extensive NO_x control experience have concluded that SCR technology is well-proven, safe, and economical now, and is characterized by decreasing costs due to technical innovations and competition among SCR manufacturers. In fact, many improvements are at hand which center on lowering the cost of SCR systems and expanding their range of industrial applications."

All of this is in sharp contrast to the situation in the U.S. where we are just beginning to cautiously install SCR units in California.

EPA Explains New Top-Down BACT Policy

As a result of top-down Best Available Control Technology (BACT) (and even tougher regulations in specific regions such as southern California and northern New Jersey), most new gas turbines in cogeneration plants must now use selective catalytic reduction (SCR) to clean the flue gas to extremely low emission levels.

Gas turbines were the first to feel the effect of this new policy, since they are the dominant form of new capacity now being permitted. It is sure to spread to all new fossil fueled generating sources as new capacity construction gains momentum. Initiated in late 1987, top-down BACT applies to the PSD or prevention of significant deterioration review required for all new sources by the 1977 federal Clean Air Act amendments. In order to obtain a PSD permit, new sources must show the permitting agency, on a case-by-case basis, that they are using the "best available control technology"—BACT— for that particular installation.

As this is being written, the U.S. Congress is finalizing the 1990 Clean Air Act. It is certain that more encouragement will be given to the ERA to move forward with their stated policy.

BACKGROUND

Techniques for accomplishing the removal of NO_x from waste gas streams and recovery for destruction of the oxides abound. Practical NO_x conversion processes usually involve the reduction of NO_x by reaction with an oxidizable material added to the gas stream. Although, in theory, it should be possible to convert NO_x to elemental nitrogen and oxygen at low temperature by dissociation according to:

$$2NO_2 \rightarrow N_2 + 2O_2 \qquad (1)$$

this reaction does not proceed below about 2,000°F at a perceptable rate, and no effective catalyst is known to accelerate the reaction significantly in the 250 to 1,000°F temperature range of interest in the treatment of flue gases from combustion processes and other high temperature applications.

The reduction processes, most of which have been known for many years, can be generally described as selective or nonselective on the basis of the reducing material used. The nonselective processes can utilize almost any oxidizable fuel such as methane, propane, butane, naphtha or other organic material. They react with oxides of nitrogen and with oxygen in a nonselective way according to the following typical reactions:

$$CH_4 + 2NO_2 \rightarrow CO_2 + 2H_2O + N_2 \qquad (2)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (3)$$
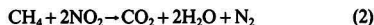
In order to achieve a relatively complete reduction of the oxides of nitrogen using a nonselective process, it is necessary to remove substantially all of the free oxygen from the gas stream. For this reason, the nonselective process has only limited applicability to combustion gases, although it may be used where the oxygen content of the flue gas is extremely low.

For abatement of the NO_2 emission problem generated by industrial processes, nonselective catalytic reduction has been used widely. Nonselective *partial* reduction takes place when a limited amount of fuel is added and a suitable catalyst is used. The NO_2 is rapidly reduced to NO with efficiencies approaching 100% when the operating temperature is sufficient to react the fuel with oxygen or NO_2 in the gas stream. Temperatures below 400°F are acceptable when hydrogen is used as the reducing gas; 600-700°F is a reasonable minimum for propane; and temperatures over 850°F are required for methane.

Selective reduction utilizing ammonia as the reducing agent with a platinum catalyst was introduced in 1963 by Engelhart Minerals and Chemicals Company. Seeking to reduce both the operating temperature and the total quantity of reducing material required for obtaining color freedom from nitric acid plant effluent, the selective reduction process substituted ammonia for the hydrocarbon reducing fuels, but utilized the same basic catalyst that had been used for nonselective reduction.

This process is workable only over a very narrow range of operating temperatures around 500°F. Operability was bounded on the lower temperature side by inability of the catalyst to carry out the ammonia oxidation reaction, and on the upper side by the tendency of platinum to generate NO_x from ammonia according to the classic reaction:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (4)$$
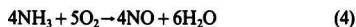
Because the reaction between ammonia and NO_x is exothermic, the amount of NO_x which can be removed using platinum catalyst is limited to 100-200 ppm. Attempts to remove greater concentrations result in increasing the temperature of the gas stream sufficiently that NO_x is actually generated by oxidation of the ammonia. This unique combination of properties of the catalyst and basic nature of the competing chemical reaction imposes two obvious limitations; first, the temperature must be carefully controlled and, secondly, the maximum NO_x concentration of the waste gas must be limited to very low levels. To these apparent disadvantages, a third more subtle one must

be added. Because operation at the low temperature level requires a very high degree of catalytic activity, the catalyst is especially sensitive to poisons. Platinum catalysts are characteristically subject to three kinds of deactivation:

1. Poisoning, by heavy metals, phosphorous, arsenic, etc.
2. Suppression, by sulfur oxides, halogen compounds, etc. plus high levels of NO_x.
3. Fouling, by dust, ash, etc.

In combination, these drawbacks limited the success of the selective catalytic reduction process for nitric acid application.

Thermal processes for NO_x reduction have not been widely used in the past. The typical applications for nitric acid plants and industrial processes would not tolerate nonselective reduction because of the high oxygen content of the gas streams and the inordinate fuel requirements which would result. Further, nonselective thermal reduction with most reducing fuels must provide an excess of fuel in order to effectively remove all of the oxygen and oxides of nitrogen.

Operation in the thermal reaction range (upwards of 1,400°F) with an excess of organic materials may result in the formation of partially oxidized byproducts such as formaldehyde, which are more serious local pollutants than are the oxides of nitrogen. The remaining alternative, selective thermal total reduction, is practical and is being applied in the design of some combustion processes currently. The principal disadvantage of the thermal NO_x reduction process is that it requires a high temperature and significant amount of residence time. In order to obtain temperatures in the 1,600°F+ range in most combustion processes, it is necessary to withdrew gas from the process while it still contains 30% or more of the heat of combustion of the fuel and pass it through a suitable reaction chamber.

The mechanical configuration of the process—whether it is a boiler, petroleum process heater, or industrial furnace—must be altered substantially in order to accommodate the residence chamber. In addition, the operating temperature is well above the ignition temperature of ammonia. Therefore, it is necessary to take some precautions to avoid simple burning of the ammonia with oxygen in the effluent stream. Thus, the thermal process is best applied to gas streams which are very low in oxygen content, such as the effluent from furnaces which have "low-NOX" burners which maintain close control of the air-fuel ratio.

The Econ-Nox process has been developed to overcome many of the disadvantages inherent in the alternative technical approaches to NO_x reduction.

The process brings together the relatively old chemical engineering art associated with catalytic selective total reduction and the hardware developed over the past 20 years by ARI for industrial pollution control reactions using fluidized catalyst beds. The final ingredient is the catalyst which permits operation over a relatively wide temperature range and eliminates the sensitivity to contaminants in the gas stream characteristic of the platinum-family catalysts.

SELECTIVE CATALYTIC NO_x REDUCTION (SCR) DEVELOPMENT

In 1971, ARI undertook a development program to produce a catalytic incineration system for oxidation of organic materials which would be free of the drawbacks inherent in the then-current catalytic, fixed element incineration systems. These systems had all but been replaced in commercial operations with thermal incinerators, because of the increasing importance of reliability in air pollution control, and the marked tendency of the catalytic systems to fall heir to poisoning. The deactivation problem, coupled with a high cost for replacement of the precious metal catalyst and the necessity to interrupt process operation to remove the spent catalyst, often resulted in continued operation of systems long after the catalyst had ceased to function properly. Thermal incineration systems did not have this drawback, and in the relatively cheap energy days, the additional cost of fuel was not too high a price to pay for increased reliability.

In the early seventies, ARI envisioned the need for a workable catalytic system which would have a significant economic advantage over thermal units. The mechanisms involved in circumventing the catalyst problems included utilizing non-precious metal catalysts of lower activity level but greater stability to minimize poisoning problems, and the use of a fluidized bed of catalyst to avoid fouling, and to permit replacement of the catalyst without interfering with the operation of the process. These requirements mandated a catalyst of greater attrition resistance than was then currently available. ARI undertook the development of the system, hardware and development of the catalyst.

Successful completion of the development program was announced in 1974, and the first commercial operation was begun in 1975 at the Chemetron (now PPG Industries) plant at Pasadena, Texas. Figure 1 is a schematic drawing of the system employed for hydrocarbon fume abatement.

Operation of the catalytic system has exceeded all of the initial targets set for the development program. In particular, catalyst attrition has been held to a level of less than 0.2 lb/million standard feet of process gas flow. This rate is far below the levels which would be permitted on the basis of air pollution emissions, and maintains a cost for replacement catalyst which is less than $1.00/mmscf. Catalyst deactivation has been almost nonexistent. Successful operations include treatment of flue gas from a lead melting furnace and emissions from several plants processing chlorinated organic materials such as vinyl chloride monomer and phosgene.

Mechanical operation of the systems has been relatively simple and trouble free. Ordinarily, operator attention is required only for startup or shutdown of the process. Several operations have been successfully carried out in which substantial quantities of dust or carbon particulate material has been present in the effluent stream. This simply passes through the bed without accumulating on the catalyst.

After several years of successful operation with the oxidation of organic fumes as the principal objective, further development work was undertaken on the burning of chlorinated hydrocarbons. In particular, vinyl chloride and ethylene dichloride are byproducts of the manufacture of vinyl chloride monomer and polymer. It was possible to burn these materials to CO_2, water vapor, and HCl at high efficiencies. Several plants are operating with guaranteed vinyl chloride monomer (VCM) levels of 5 ppm. All of these plants are running below their performance guarantees.
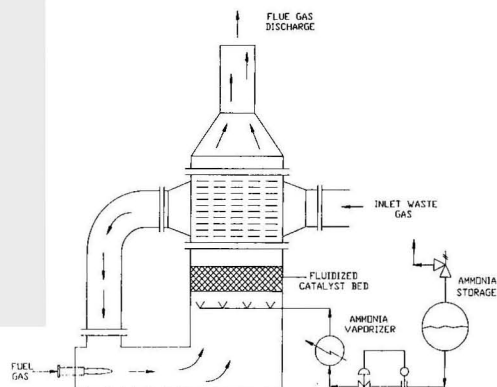
FIGURE 1. Schematic flow diagram of Econ-Nox™ selective catalytic reduction system
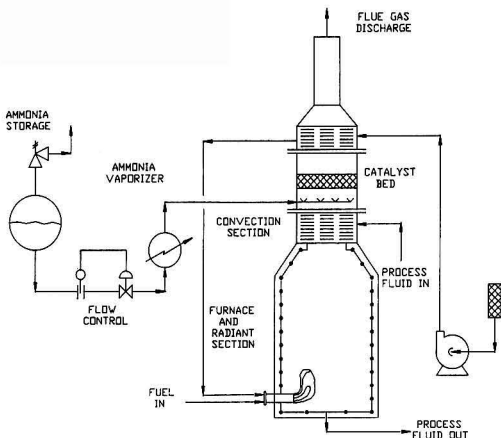
FIGURE 2. Process heater with Econ-Nox™ NOₓ reduction section

In 1979, several applications arose in which the ability to oxidize ammonia without cogeneration of NO_x appeared. Development work was aimed at establishing a catalytic system which could dispose of the unwanted ammonia without generation of NO_x and could be carried out over the temperature range of about 500°F to as high as 800°F. These units have been installed in west coast refineries for the treatment of waste gas.

The next logical step in the evolution of the Econ-Nox(TM) process involved coupling the technology developed nearly twenty years ago, to provide a workable, efficient process where the reduction of NO_x present in the effluent of process heaters, steam boilers, gas turbines and utility electric plants and other major combustion sources.

Traditionally, as commercial pollution control technologies have evolved, and experience is gained, the cost of that technology has been reduced. For example, in Japan and West Germany SCR costs have been lowered considerably over the past ten years. If NO_x emission standards are established which required the use of SCR control technology in the United States, a major part of the technology development effort will focus on reducing the cost of control.
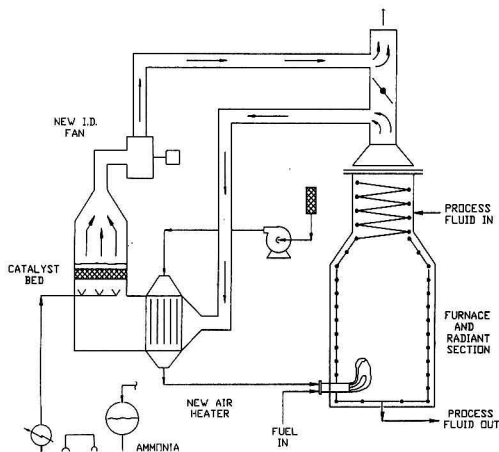
FIGURE 3. Existing process heater with retrofit NOₓ reduction section and air preheater.

Burner Modifications

Bias Fuel and Air	30%
Overfire Air (OFA)	30%
Low NOx Burners (LNB)	40–60%
Reburn	50%
Low NOx Burner + Reburn	70%

Post Combustion

Selective Catalytic Reduction 85–90%

$$GHSV \propto \frac{1}{\left[\overline{NO_X}\right]^{0.5}_{INLET}}$$
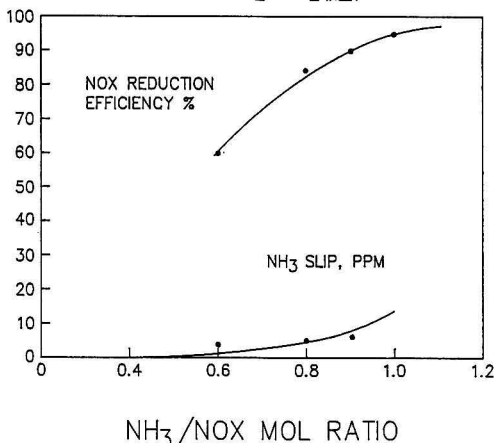
FIGURE 4. NOₓ emission reduction.

SYSTEM DESCRIPTION

Although the chemistry of the selective reduction reaction and of the catalyst are complex, the physical system is extremely simple. In fact, most of the elements ordinarily included in a catalytic incineration system for the control of organics, chloro-organics or ammonia, can be omitted when the process is applied to a flue gas stream.

Figure 2 is a diagram illustrating the adaptation of the Econ-Nox catalytic system to a new refinery process heater. In this case, air preheat is required to provide a thermal efficiency acceptable by current standards. The catalytic NO_x reduction system is located after the convection section of the heater, but before the air preheater. The mechanical equipment consists of a housing, catalyst support grid and catalyst bed, and an ammonia metering vaporization and injection system.

Figure 3 illustrates a similar system retrofit to an existing heater downstream of the convection section of a steam boiler designed for oil field use.

In both these cases, the oxides of nitrogen concentration is relatively low; less than 150 ppm for the case of the refinery gas-fired process heater, and less than 300 ppm for the oil field steam generator using crude oil as fuel. In both cases, the temperature change across the catalyst bed is on the order of 5°F, which approximately offsets the heat loss due to radiation.

Existing boilers and process heaters can be treated by this method as illustrated. Operating characteristics of the system are tabulated as follows:

Gas Flow, SCFS/FT^2	3.0
Gas Hourly Space Velocity	5–10,000
Pressure Drop, Inches Water Column	8–10
Ammonia/NO$_x$, Mole Ratio	0.8–0.9
Expected NH$_3$ Conversion, %	>99
Expected NO$_x$ Conversion, %	>85

The operating limits of the system at present are as follows:

Minimum Temperature, °F	550
Maximum Temperature, °F	750
Maximum NO$_x$ Concentration, ppm	2,000

No limits are specified for oxygen concentration as it is assumed that it will be at least 2 mole percent. Some of the operating limitations, for instance, with respect to upper temperature limit, may be removed as the development of the process progresses.

SUMMARY

The Econ-Nox process represents an orderly development from the thermal and selective catalytic NO$_x$ reduction system of two decades ago (Figure 4) using hardware developed for treatment of gas streams contaminated with organics, and coupled with a superior catalyst. The present system has a number of unique characteristics including:

1. Broad operating temperature range.
2. Resistance to poisoning, suppression and fouling which characterize precious metal catalyst systems.
3. A nonprecious metal, relatively inexpensive catalyst.
4. A well demonstrated, trouble free mechanical system.
5. Low pressure-drop, operating and maintenance costs.

It is a new application for old and well demonstrated process elements.

CONCLUSION

Combustion modifications are in use in the U.S. in over 135 installations for the reduction of NO$_x$. Reductions of 50% are routinely obtained. Combinations of combustion methods such as low NO$_x$ burners and reburning have also been applied. These are reported to achieve 70–75% NO$_x$ reduction. No coal firing operation in the U.S. currently uses SCR-Selective Catalyst Reduction although it is used in several oil-fired units.

Currently, all U.S. boilers must comply with the Clean Air Act NO$_x$ requirements.

The Econ-Nox uses a fluidized catalyst bed to accomplish selective total reduction of oxides of nitrogen to elemental nitrogen using ammonia as the reactant fuel. The process can be designed for operating temperatures between 500°F and 800°F and for a wide range of operating variables as oxygen concentration, sulfur dioxide content and moisture content of the gas being treated.

The SCR process brings together some old technology on the selective reduction chemistry, relatively new fluidized bed incineration techniques and a new, nonprecious metal, Econ-Acat catalyst which permits operation over a broader temperature range than has been practical in the past.

Stringent regulations on NO$_x$ emission make application of the Econ-Nox process economically attractive for refinery and industrial process heaters, boilers, and gas turbine stations.

LITERATURE CITED

1. Hollinden, Jerry, *McIlvaine Air Pollution Management Newsletter, No. 138*, Northbrook, Illinois, pg. 2 (November 1989).
2. "Selective Catalytic Reduction (SCR) Controls to Abate NO$_x$ Emissions," *Industrial Gas Cleaning Institute (IGCI) white paper*, Washington, D.C., (July 1989).
3. Kosusko, M., and C. M. Nunez, "Destruction of Volatile Organic Compounds Using Catalytic Oxidation," *Air & Waste Management, Vol. 40, No. 2*, Pittsburgh, Pa., pg. 254 (February 1990).
4. Nagl, G. J., and L. C. Hardison, "Reduction of Nitrogen Oxide Emissions From Calciners," U.S. Patent No. 4,40-2,273, U.S. Patent Office, Washington, D.C., (1983).
5. Ulrich, B., "Waldsterben Forest Decline in West Germany," *Environmental Science Technology, Vol. 24, No. 4*, American Chemical Society, Washington, D.C., pg. 436 (April 1990).
6. Lyons, C. E., "1987–8 Denver Brown Cloud Study," *Chemical Engineer Progress*, University of Denver, pg. 61 (May 1990).
7. Addison, G. E., F. M. Nooy, and R. L. Verson, "The Shell Flue Gas Treating Process: Recent Evaluation of Non-Polluting Pollution Control," UOP Process Div., UOP, Inc., Des Plaines, Illinois, 1978.

Potential Problems Using the TCLP to Determine BDAT Compliance

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A major result of the Land Disposal Restrictions (LDR) is that all listed hazardous wastes must be treated prior to land disposal. When evaluating treatment options, generators will want to know whether the treated waste meets the Best Demonstrated Achievable Technology (BDAT) criteria for land disposal. To avoid enforcement action and penalties, analytical data must confirm that the treated waste meets BDAT criteria.

Many BDAT criteria are based on the constituent concentration in the Toxicity Characteristic Leaching Procedure (TCLP) extract of the waste. Since the TCLP uses an acidic solution to leach the waste constituents, reported results may be influenced by hydrolysis, interfering compounds or laboratory contamination. Sufficient quality assurance samples must be analyzed for the data to be court defensible.

This paper proposes methods for minimizing analytical problems and obtaining representative data. A case history illustrates several of the problems and related solutions.

INTRODUCTION

The EPA Land Disposal Restriction (LDR) Program (40 CFR 268) includes treatment standards for each of the wastes banned from land disposal. The treatment standards are expressed as either waste concentrations or as concentrations in the waste extract. Constituent concentrations in the waste (CCW) are determined by using *Test Methods for Evaluating Solid Waste* (SW-846). The new Toxicity Characteristic Leaching Procedure (TCLP), which replaces the Extraction Procedure must now be used to produce an extract if the treatment standard is based on the constituent concentrations in the waste extract (CCWE).

The final rule which describes the TCLP also finalized the Toxicity Characteristic (TC) for hazardous waste and lists the

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twenty-five organic chemical parameters. Thus, the TCLP may be used either to determine whether a waste is hazardous or to determine whether a treated waste meets the BDAT criteria for land disposal. It is interesting to note, however, that most organic compounds listed as parameters in the waste treatment standards are not included as TC parameters. Supplementary information and comments published with the final Toxicity Characteristic Rule indicate that a number of organic compounds were deleted from the TC parameter list because they were susceptible to hydrolysis, adsorption, and biodegradation during transport through the aquifer. In other cases, it may also be difficult, using EPA approved methods, to obtain the analytical detection limits required by the BDAT criteria.

A major result of the LDRs is that hazardous wastes will increasingly be treated to meet the BDAT criteria for land disposal. Both profitability and EPA enforcement will cause disposal companies to strictly enforce the LDRs. Thus, the quality of analytical data confirming the BDAT criteria will become increasingly important.

ANALYTICAL RESULTS MAY BE MISLEADING

The TCLP is designed to evaluate the mobility of both organic and inorganic waste constituents. The older Extraction procedure was only used for inorganics, pesticides and herbicides. The 25 organic, nonpesticide, nonherbicide compounds now listed as Toxicity Characteristic parameters are the focus of this discussion.

For soils, sludges and samples containing greater than 5% solids, the TCLP uses an acidic solution to extract the waste constituents. For all volatile wastes and wastes with a pH less than or equal to 5.0, the extraction fluid is a buffer of acetic acid and sodium hydroxide adjusted to a pH of 4.93 ± 0.05. For wastes with a pH greater than 5.0, a dilute solution of acetic acid is used. The pH of this solution is adjusted to 2.88 ± 0.05. The extraction fluids must be made up using ASTM Type II Water to dilute the concentrated acid and buffer solution to the correct concentration.

Any of the extraction fluid constituents (acetic acid, sodium hydroxide, or water) may be the vehicle for contaminants. Esters and ketones are byproducts of the reactions which produce acetic acid and trace amounts may be present in the stock solution of the acetic acid. The use of ACS reagent grade glacial acetic acid from a reliable supplier will minimize this possibility. Trace amounts of volatile organic compounds may remain in the reagent water used for dilution. Proper preparation and storage can avoid this problem. Prior to sending samples to a laboratory, an independent audit should be performed to assure that proper quality reagents are being used and that reagents are properly stored prior to use in TCLP analyses.

Reactions of waste constituents with the extraction fluid may produce compounds other than those originally present in the waste sample. The final rule describing TCLP (55 FR 11798, March 29, 1990) deleted several compounds from the Toxicity Characteristic (TC) list provided in the proposed rule (51 FR 21648, June 13, 1986). The proposed rule was to cover an additional 13 chemicals. These are listed in Table 1, which also provides the reason the particular chemical was not included in the final rule. Seven chemicals were not included because they exhibit a high degree of chemical reaction with water. EPA's subsurface fate and transport model used to determine the regulatory levels does not adequately model these chemicals and EPA does not have adequate toxicity data on the hydrolysis products. The remaining six deferred chemicals are those for which the required steady state model employed in the analysis does not properly model their fate. Their existence is too transient for the model. One of the reasons given for deleting a compound was that it hydrolyzed in water. Although these compounds have been deleted from the TC list they have not been deleted from the BDAT parameters lists. For example, methylene chloride, carbon disulfide, and toluene are BDAT parameters for F001 and F005 wastes. These compounds may react with or be hydrolyzed by the extraction fluid to produce other compounds that are BDAT parameters.

In other cases, the BDAT parameters include a constituent for which there is no EPA-approved method of analysis. For instance, the BDAT parameters for F-solvent wastes (F001 to

F005) include methanol. Not only is there not an SW-846 method for the analysis of methanol in a waste sample, but the methods available have detection limits above 0.75 mg/l. Thus, it is not possible using SW-846 or other EPA-approved methods to document that the TCLP extract meets the BDAT criteria for land disposal.

One way around the problems of reaction products or high detection limits is to analyze an unextracted sample for total constituent concentration. A careful reading of the TCLP indicates that this is a permissible strategy. On the other hand, this does not allow for the 20-fold dilution of the TCLP methodology, or low solubility in water due to strong adsorption to the soil. In the event that total constituent concentrations are determined, they must be less than the BDAT criteria. In some cases, negotiations with regulatory agencies may permit an allowance for dilution. However, due to financial considerations and regulatory liabilities, disposal companies seldom, if ever, make such allowances.

Finally, the acetic acid in the extraction fluid degrades the packing/coating material in the GC/MS column. Labs must change columns often before degradation products (siloxanes) become a nuisance and obscure the spectra. The use of a good quality lab is the best solution to this problem.

QUALITY ASSURANCE FOR DEFENSIBLE DATA

The hazardous waste regulations for land banned wastes (40 CFR 268) require that, prior to land disposal, the generator determine if the subject waste meets the BDAT criteria. To forestall the possibility of costly enforcement actions, the determination should be based on analytical data which are defensible in the event of future litigation.

Defensible data require a good quality control (QC) program and good quality assurance (QA) procedures. The goal of the quality control program is to control errors and to verify that analytical methods are operating within acceptable performance limits. The use of qualified personnel, reliable and well-maintained equipment, appropriate calibrations and standards, and close supervision of all operations are important components of a QC program.

A QC program involves both field and laboratory procedures. Field procedures include sample collection and handling. Laboratory procedures include sample receipt, storage and analysis. Specific areas of concern in field QC include sampling and handling techniques; documentation of prefield, field and postfield activities; and generation of QC samples such as field duplicates, trip blanks, field banks, and equipment blanks. SW-846 mandates that documentation of compliance with these requirements be maintained and available upon request.

Analytical laboratory QA procedures are designed to monitor the quality of the analytical data being produced. The laboratory QC program requires:

- use of matrix spikes and surrogates to determine that the required sensitivity is achieved;
- periodic analysis of duplicate samples;
- analysis of field QC samples to show that the sample is free from contamination errors introduced in sampling and handling;
- use of standard curves and check samples to indicate proper instrument calibration; and
- use of detection and quantification limit criteria to show that the method detection limit was adequate to detect analytes at or below a regulatory threshold and assist in the identification of possible sources of error and laboratory problems.

The generator should be aware that when the TCLP is involved, a quality assurance sample (such as matrix spike) should be run for each type of sample, rather than the typical 1:10

Table 1 Proposed Constituents Not in Final Rule

Reason For Not Including	
Chemical Reaction	Fate Model Improper
Acrylonitrile	Carbon Disulfide
bis(2-chloroethyl)ether	1,2-Dichlorobenzene
Methylene Chloride	Isobutanol
1,1,1,2-Tetrachloroethane	Phenol
1,1,2,2-Tetrachloroethane	2,3,4,6-Tetrachlorophenol
1,1,1-Trichloroethane	Toluene
1,1,2-Trichloroethane	

Table 2 Rolloff Box Soil Analysis and BDAT Criteria

PARAMETERS,	BDAT	BOX #1-197-20		BOX #2-230-30		BOX #3-266		BOX #4-T3154		BOX #5-3137		BOX #6-T2052		Detection Limit	
concentration	ug/L	Total	TCLP	Total	TCLP	Total	TCLP	Total	TCLP	Total	TCLP	Total	TCLP	Total	TCLP
Acetone	590	16	16,000/3,100	ND	2,200/2,500	ND	840	ND	1,900	ND	860	ND	470/2,000	10	50
n-Butanol	5,000	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	1,300
Carbon Disulfide	4,810	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5	50
Carbon Tetrachloride	960	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5	25
Chlorobenzene	50	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	5	25
Cyclohexanone	750	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	25	1,500
Ethyl Acetate	758	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5	25
Ethylbenzene	53	ND	ND	65	ND	84	ND	ND	ND	ND	ND	13	41/25	5	25
Ethyl Ether	750	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5	25
Isobutanol	5000	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	50	250
Methylene Chloride	960	8	990/5,700	8	940/1,800	ND	590	7	3,500	ND	540	ND	6,600/1,000	5	25
Methyl Ethyl Ketone	750	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	50
Methyl Isobutyl Ketone	750	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	50
Tetrachloroethylene	330	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5	25
Toluene	330	9	40	9	40	ND	40	13	ND	23	77	23	ND/310	5	25
1,1,2-Trichloro-1,2,2-Trifluoroethane	960	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	5	25
1,1,1-Trichloroethane	410	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	5	25
Trichloroethylene	91	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	5	25
Trichlorofluoromethane	960	NA	ND	2,800	ND/250	13	1,100	ND	ND	ND	ND	12	130/86	5	25
Xylene (total)	150	NA	ND	ND	ND	NA	ND	NA	ND	NA	ND	5	ND	5	25
Methanol	750	NA	910,000	NA	790,000	ND	540,000	ND	3,300,000	ND	3,000,000	NA	1,100,000	500,000	500,000
1,2-Dichlorobenzene	125	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	10
Nitrobenzene	125	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	10
Pyridine	330	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	10
o-Cresol	750	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	10
m-Cresol	750	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	10
p-Cresol	750	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA	10

Notes:
NA = Not Analyzed
ND = Not Detected
Total concentrations are in ug/Kg and TCLP concentrations are in ug/L.
When duplicate samples were analyzed, reported values are separated by a "/".

or 1:20 ratio. This means that if one sludge sample and one soil sample are submitted for analysis, the laboratory should analyze two matrix spikes, one for each media type. This documentation is especially important in documenting proper disposal of each of the two treated wastes. If documentation were inadequate, penalties for the land disposal of inadequately documented (that is, still hazardous) waste could be substantial.

CASE STUDY—SOLVENT CONTAMINATED SOIL

In the course of closing hazardous waste units at a paint plant, six rolloff boxes of contaminated soil were generated. Samples had previously been collected from the waste units and the analytical results indicated that the total waste constituent concentrations were less than 20 times the BDAT criteria. Thus, it appeared that, following the 20-fold dilution of the TCLP, the parameter concentration in the extract would be less than the required BDAT criteria.

The soil had been contaminated by F001 to F005 solvents. The constituent concentrations for BDAT are listed in Table 2. To take advantage of the dilution factor and contain project costs, the lab was instructed to analyze the TCLP extract for the parameter list. The results are tabulated in Table 2. According to these results the concentrations of acetone, methanol, methylene chloride, ethylbenzene and xylene exceeded the BDAT criteria and the soil could not be landfilled.

Subsequently, the soil in the rolloffs was resampled and analyzed for the total concentration of the parameters. The total concentration results indicated that only rolloff 2 required incineration and resulted in savings of $60,000. These later results also caused us to question the laboratory about the source of the methanol, methylene chloride and acetone. It was determined that the lab was rinsing the extraction jars with methanol at the conclusion of the cleaning process. It seems that the methylene chloride and acetone are byproducts of methanol production. Laboratory personnel had assumed that the methanol and any traces of byproducts evaporated during air drying of the extraction container. However, these results clearly indicate that part per billion analyses will detect very low concentrations and that the 20-fold dilution magnifies the effect of trace solvents on the laboratory glassware.

In this case only one set of QA samples was necessary because all the samples were soils. These samples were run in a high quality laboratory. Earlier that year the laboratory's personnel had performed Contract Laboratory Program (CLP) analyses on approximately 50 samples from a site proposed for inclusion on the National Priority (Superfund) List. The resulting data had been 100% valid and two laboratory audits had noted only insignificant problems, which were remedied.

The problem described above was due to the newness of the method. The laboratory was trying to minimize the possibility of cross contamination through the use of the methanol rinse. Although glassware rinsing is not described in the TCLP methodology, it is not prohibited.

CONCLUSION

Problems may be encountered when the TCLP extract of a waste sample is analyzed. The problem of trace contaminants in the reagents can be remedied by using a quality lab. Through experience, good labs should now have eliminated the use of final equipment rinses with organic solvents.

The problems of hydrolysis by and reaction with the extraction fluid can only be solved by analysis for total concentration so that water and acid are not introduced into the sample. QA/QC procedures should be written into the work plan. Written procedures and experience in sampling will provide good field QA. Laboratory QA/AC should be explored verbally with the lab when analytical costs are provided. A copy of the lab's written QA/QC program should also be requested at this time.

Determination that a waste meets BDAT criteria carries significant liability. Samples of this importance should only be sent to a laboratory which has previously provided consistently acceptable results. It is important to communicate project needs to the lab personnel and provide them as much information as possible about the samples submitted, and about how the data will be used. Finally, any lab used routinely for RCRA related samples should be audited periodically to ascertain that quality is maintained.

NOTE

Since completion of this paper, the EPA has requested data and comments concerning revision of the treatment standards for nonwastewater F001–F005 spent solvent wastes. The advance notice of proposed rulemaking notes that the Agency is considering establishing treatment standards for these wastes based on the analysis of total constituent concentrations as an option for compliance with existing leachate standards.

LITERATURE CITED

U.S. Government, *Code of Federal Regulations* 40 CFR 268.
U.S. EPA, *Federal Register*, March 19, 1990, 55, (61), 11798.
U.S. EPA, *Federal Register*, May 30, 1991, 56, (104), 2444.

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