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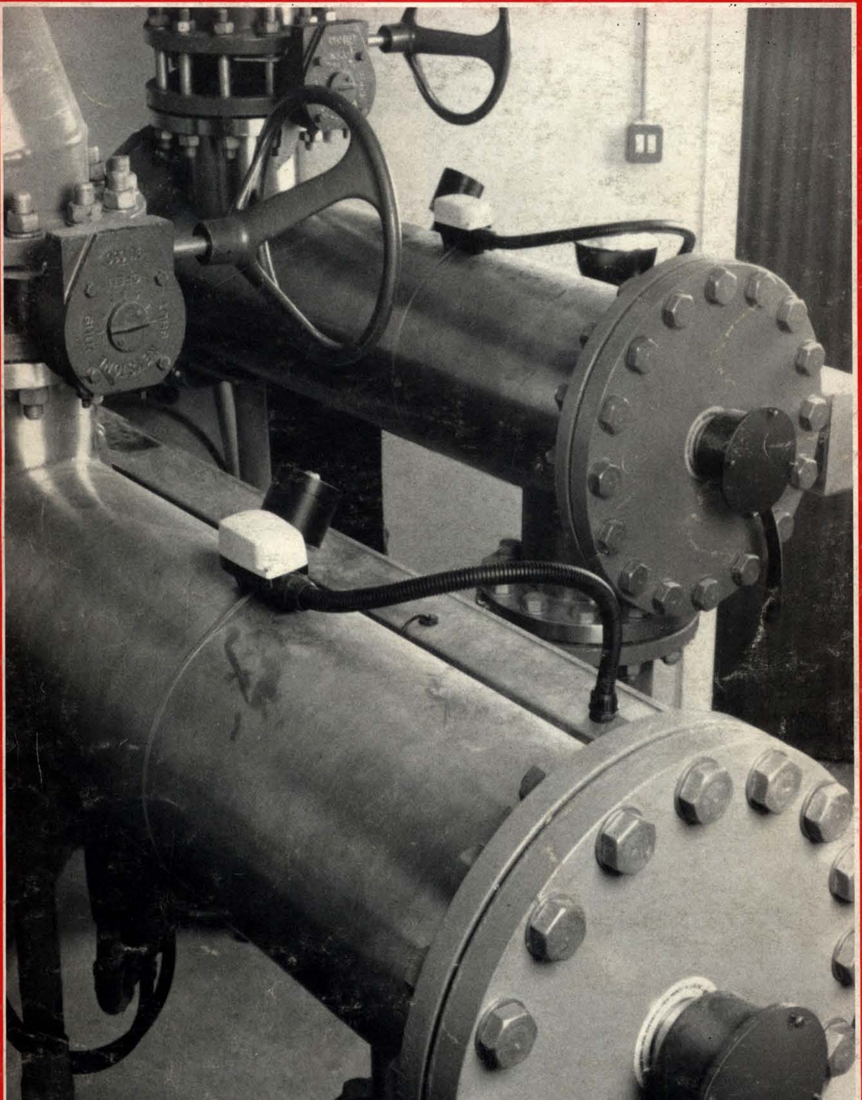
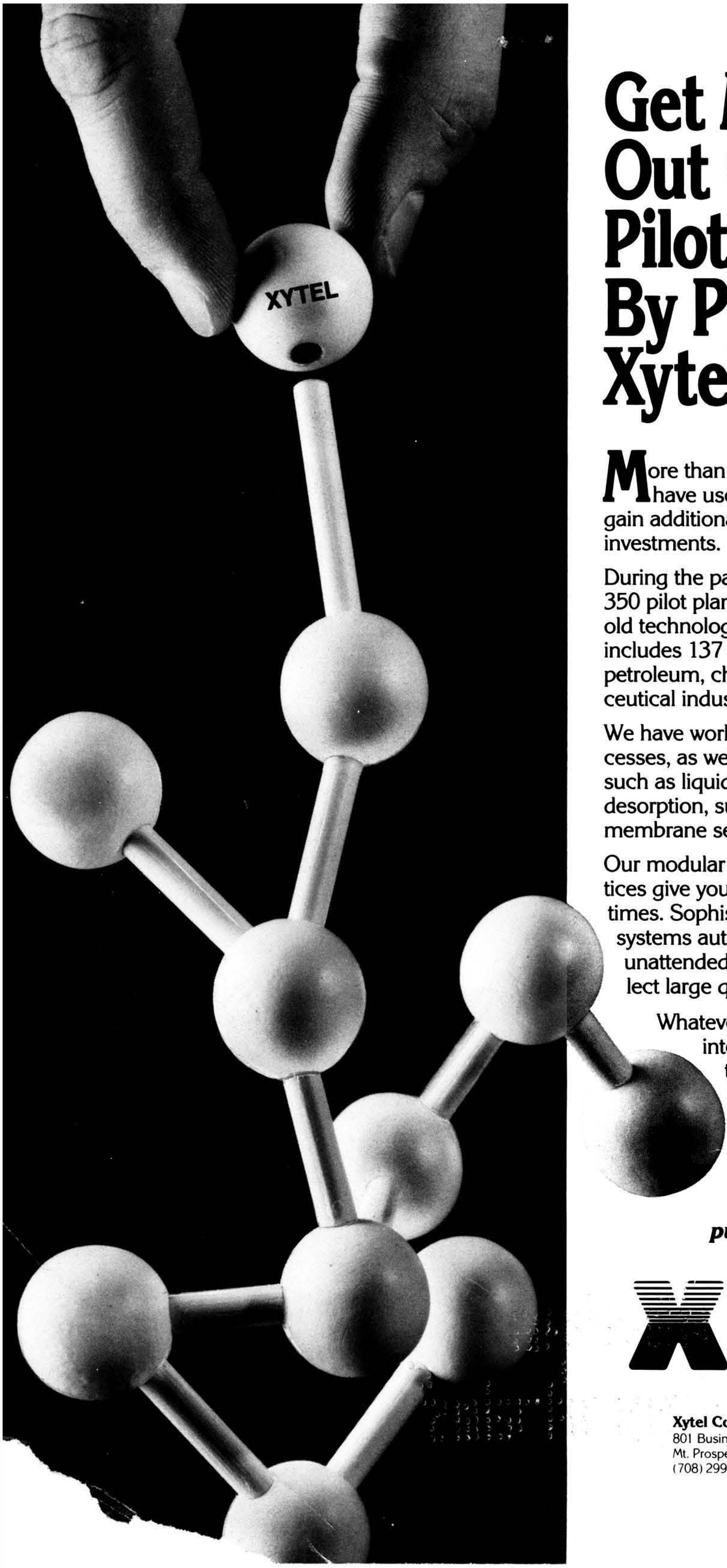


Process and plant water disinfection unit with ultraviolet light.
Photo courtesy of Aquionics Inc., Erlanger, Kentucky.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ENVIRONMENTAL PROGRESS

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

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Caught in the Middle: Right-to-Know from a State Perspective

Richard L. Shank

A decade ago, anyone who worked with chemicals probably assumed the really nasty toxic stuff wasn't in their backyard.

All that changed in 1984 when more than 2,000 people died in Bhopal, India, as a result of an accident at a nearby pesticide manufacturing facility. Afterward, people asked, "Could Bhopal happen here?" And, many times, the answer from government officials was, "We really don't know." Health, environmental, and safety agencies had surprisingly little information about the multitude of chemicals used and produced in their communities. To their chagrin, citizens found that the release of some of these compounds was neither monitored nor regulated. Around that time, a cyanide release in Institute, West Virginia, brought the problem to Washington, D.C.'s backyard and spurred Congress to act.

The Emergency Planning and Community Right-to-Know Act takes an important first step toward informing the public of the existence of chemicals in their neighborhoods. Passed by Congress in 1986 as part of the Superfund Amendments and Reauthorization Act, the federal program requires facilities that store, use, generate, or release hazardous materials to report the materials' identity, chemical properties, storage location and volume to local, state and federal authorities. In turn, local planning committees must use this information to prepare plans to deal with emergencies involving these hazardous substances. Both reports from companies and the community response plans are available to the public for review. As chair of Ohio's State Emergency Response Commission, Ohio EPA has the difficult task of coordinating implementation of this legislation at the local level.

We're three years into the program, and we're beginning to get some perspective. In this instance, the federal government mandated a new program, but provided no funds to administer it. As a result, we had to get the Right-to-Know program up and running on a shoestring. And, I'll be honest, we're only beginning to dig ourselves out from under the paper—the thousands of chemical inventories that have to be organized and filed by too few staffers.

The Right-to-Know program is changing the way we look at Ohio industry, which is all for the good. Nevertheless, the lack of sufficient funds, inadequate staffing and the need to set new state rules have contributed to our growing pains.

On the most general level, does the program really provide the information local responders need? For instance, the Right-to-Know program originally intended to gradually reduce the threshold amount of chemicals that companies must report to 500 pounds. However, largely due to industry pressure, the reportable quantity will remain at 10,000 pounds for hazardous chemicals. That still leaves a lot of chemicals sitting around out there that we—and local safety officials—don't know about. I'm not sure that quantities below 10,000 pounds are "safe enough" for our firefighters to be unaware of their presence.

Even with that 10,000-pound reporting threshold—which implies that we're dealing only with fairly large operations—our ability to find these companies and make sure they report is very limited. As in a number of other states, the fees companies pay when they submit their reports provide the funds to help administer the program at the state and local levels. When fees were set, we estimated that, given the number of companies likely to report 500 or more pounds of chemicals, we would collect $5 million to run the program. This year, we've collected $600,000 and the threshold remains at 10,000 pounds. Moreover, although we have funding problems, Ohio is ahead of many states in that we have passed our own Right-to-Know legislation that generates fees for the program.

We believe only about 40 percent of Ohio companies that should report have done so. But without the necessary funds to hire staff, Ohio EPA is unable to bring non-complying companies into the fold. The Local Emergency Planning Committees have the authority to enforce reporting regulations, but they too have limited funds and staff.

An important part of the Right-to-Know program is the section involving emergency planning. The law requires that every community have a plan that enables emergency responders, health and safety officials, and law enforcement agencies to respond to emergencies involving chemicals. The chemical inventories companies submit are used to design these plans. In Ohio, like many other states, the planning groups, known as the Local Emergency Planning Committees, are organized on a county-by-county basis. Statewide, more than 3,000 people participate in the local planning committees.

One problem lies with the program's expectations. Congress envisioned these Local Emergency Planning Committees to be voluntary organizations in which local government, industry, citizens and the media cooperated to prepare the plans. However, the manuals outlining the way the plans are to be written are extremely technical. It is just too much to expect a Local Emergency Planning Committee in a rural county—where the firefighters are volunteers and volunteers with technical expertise are scarce—to dig through these complex, time-consuming instructions. The committee members have the demands of their daily jobs pressing on their time. Seven Ohio counties still have no plans.

Looking beyond these problems, a lot of good has come out of the Right-to-Know program. Watching the Local Emergency Planning Committees rehearse their plans in exercises has opened my eyes, and many others', to the difficulty of maintaining good communications between all the agencies involved during an emergency situation. Developing this teamwork will pay off in times of crisis.

We're also seeing the "buddy system" in action. It takes expensive equipment, as well as highly trained staff, to respond to some emergencies. As a result of working together on these plans, more communities are pooling their resources. For instance, when one fire company owns a foam truck and another owns self-contained breathing units and an air truck, they now are joining forces to make a team that neither community could afford to maintain on its own.

For our part, Ohio EPA's Emergency Response Section will continue to help out at the scene of environmental accidents and spills. Now that we're getting used to dealing with the annual reports, we can focus more of our attention on the needs of the Local Emergency Planning Committees. We all can benefit from better industry compliance; and Ohio's regulations are written in a manner that if a Local Emergency Planning Committee takes enforcement action against a violator, the committee can keep the money from the settlement. To help, we're working on a program to train firefighters to spot potential violators when they conduct routine inspections. In Columbus, the firefighters' training school has conducted such a course.

All told, the majority of chemical emergencies happen at small business operations across the state. Unfortunately, these are the businesses who are least likely to have consultants or specialized staff to help them comply with reporting requirements. Many of them don't even know they are required to report. Since the guy who buffs the finish at a plating operation may well be the guy stuck with filling out the forms, our next task is to design material that is easy enough for a person with no technical training to follow. When nonspecialists are aware of Right-to-Know, and understand why it is important for them to participate, we will have made a significant improvement in the safety of our communities.

***Richard L. Shank**, Ph.D., is Director of the Ohio Environmental Protection Agency, Columbus, Ohio.*

Lawrence Ross Named Director of Center for Waste Reduction Technologies

Lawrence L. Ross has been named staff director of the Center for Waste Reduction Technologies, which the American Institute of Chemical Engineers (AIChE) established late last year. In making the appointment, Richard E. Emmert, AIChE's executive director, said Ross will bring "valuable experience in technology transfer; industry, academic and government relations; and strategic planning" to the job. Ross assumed the position on May 30.

Ross comes to the new center from the National Science Foundation Engineering Research Center for Hazardous Substance Control at the University of California at Los Angeles. As its executive director, he has overseen cross-disciplinary research and education projects and been responsible for technology transfer and outreach—providing the link between the center and its 40 industrial and government affilitates.

In accepting the appointment, Ross said: "Over the past decade, as public demands to reduce wastes have grown, concerned executives and government officials have come to realize that traditional approaches to pollution control must give way to a new generation of clean technologies which focus on waste prevention." He added: "The AIChE center provides an exciting forum for synergistic linkages among groups like UCLA's center, other research facilities, industry and government agencies."

Previously, Ross was group vice president for research and development with Kinetics Technology International Group in Monrovia, California. Earlier, he spent 18 years on the staff of Santa Fe Braun Corporation in Alhambra, California, most recently as manager of advanced technology.

Ross, an AIChE member, earned his doctorate in chemical engineering at McMaster University in Hamilton, Ontario, Canada. He received his master's and bachelor's degrees in chemical engineering from the University of Toronto. He has also been awarded a certificate in business management from the University of California at Los Angeles.

The Center for Waste Reduction Technologies is serving as a focal point for waste reduction research and technologies which can provide economic and social benefits to a broad range of industries and the public. The center is working to identify research needs and priorities in process modification and change, materials substitution, and internal recycling. It will sponsor targeted research through university and other research facilities and communicate the information it develops in publications, conferences, continuing education programs and an information clearinghouse.

The center has offices in New York and Washington. For further information, contact the Center for Waste Reduction Technologies at 345 East 47th Street, New York, New York 10017 (212/705-7660) or at 1707 L Street, NW, Suite 333, Washington, DC 20036 (202-223-0650).

Congress Urged to Focus on Non-Hazardous Waste Issues

A spokesman for the chemical industry recently urged Congress to focus on recycling and non-hazardous waste issues as it works to reauthorize the Resource Conservation and Recovery Act, the law that determines how solid wastes are handled.

Morton L. Mullins, director of regulatory affairs for the Monsanto Company, was testifying for the Chemical Manufacturers' Association before the House Transportation and Hazardous Materials Subcommittee on three RCRA reauthorization proposals. He said that for RCRA to work better, CMA supports:

- ensuring that a credible program exists for managing non-hazardous wastes in all states;
- encouraging pollution prevention, resource conservation and recycling activities; and
- simplifying the existing statutory and regulatory program so that it is more readily understood, implemented and enforced.

Mullins warned, however, that the bills under consideration "overshadow these critical recycling and non-hazardous waste management issues with far-reaching and unnecessary expansions in the hazardous waste area." He voiced CMA's fears that, "amendments to hazardous waste programs will completely overshadow and divert resources from the non-hazardous waste program." The chemical industry currently manages considerably more non-hazardous waste, he added.

Washington Environmental Newsletter

Clean Air Act—Update
On July 13 the first House-Senate meeting on clean air legislation took place, but only 40 of the 150 legislators named to the conference attended. The Senate conferees offered compromise provisions on permitting and CFCs. House conferees did *not* respond to these provisions, nor did they agree on a data for the next meeting. As we predicted earlier, passage of a new Clean Air Act will probably be delayed until the late fall of this year.

R&E Tax Credit Increases
The Council on Research & Technology recently announced that the restructured tax credit will increase incentives to spend monies on research and experimentation by a factor of four times the amount spent in 1989. The study, "The Incentive effects of the New R&E Tax Credit," estimates a $25.7 billion increase in R&E spending from 1991-1995.

RCRA Reauthorization
The House Subcommittee on Transportation and Hazardous Materials was scheduled to begin mark-up of RCRA reauthorization in late June. The mark-up session has been repeatedly delayed as a result of House activities on the Clean Air Act amendments, and we question whether Congress will have time to deal with RCRA legislation this year, although Congressmen Luken remains committed to proceeding, since he is retiring at the end of this session. Senate Majority Leader Mitchell has stated publicly what many observers have been saying privately—that Congress would not pass RCRA until next session.

The key House bills are HR 3735, HR 3736 and HR 3737—all introduced by Congressman Tom Luken who serves as Chair of the House Subcommittee.

Diesel Emissions and Cancer
EPA has released a draft document, "Health Assessment Document for Diesel Emissions," which supports earlier data that diesel emissions are linked to cancer. The EPA hopes that these findings will influence congressional action on the clean air bills.

U.S.-Canadian Talks on Air Pollution
On August 28th, U.S. and Canadian representatives will meet to discuss an Air Quality Accord to manage transboundry air pollution. This will be the first significant agreement between any two countries to address environmental problems.

Industry/Government—Technology Sharing
Energy Secretary Watkins has signed agreements to allow private industry to share technology developed by government labs. The agreements resulted from the 1989 "National Competitiveness Technology Transfer Act" that was promulgated to increase U.S. competitiveness by forming partnerships between industry and government. As Sen. Albert Gore (D-TN) stated, "If America's manufacturing facilities had a fraction of the expertise and knowledge that exists at our national labs, we could leapfrog the Japanese and Europeans, . . ."

EPA Deputy Administrator Names Pollution Prevention as Key Issue
F. Henry Habicht, Deputy Administrator of the U.S. EPA recently stated that the nation's number one environmental issue is "compartmentalization," that is, our tendency to subdivide the environment into individual programs such as air, water, waste etc. Pollution prevention must be integrated into everything we do. It is the key to a systematic approach to environmental protection. EPA and DOE are very supportive of the goals and objectives of AIChE's Center for Waste Reduction Technologies, and recognize that it can play a major role in bringing about significant progress in the area of pollution prevention.

This material was prepared by AIChE's Washington Representative, Siegel • Houston & Associates, Inc.
Suite 333, 1707 L Street, N.W., Washington, D.C. 20036. Tel. (202) 223-0650

Book Reviews

Indoor Air Pollution Control by Thad Godish, Lewis Publishers, Inc., Chelsea, MI (1989), 401 pages [ISBN No.: 0-87371-098-3] U.S. List Price: $59.95

One of the involuntary actions that is constantly taking place throughout our lives is breathing, i.e., breathing the air around us. An individual typically spends about 90% of the time indoors. Hence, indoor air quality should be a top priority. Current standards, however, primarily regulate outdoor air quality.

Indoor air quality is an emerging concern and is, therefore, a "new kid on the block." High radon levels in homes, nonsmokers suffering ill health from environmental tobacco smoke, sick building syndromes, and Legionnaire's disease mysteriously killing guests at a convention hotel have heightened citizen awareness and attention to the problem of indoor air pollution.

Indoor air pollutants may contain substances generated by the occupants or their activities, objects within buildings, building design, or the structure itself. The indoor air pollutants are typically one or more among radon, formaldehyde, volatile organic compounds, asbestos, environmental tobacco smoke, pesticides, biological contaminants, and combustion products. Indoor air pollution is a growing problem. Its health effects range from a nuisance to irritation to death, depending on the pollutant, its concentration, and length of exposure. Little is known about long-term low level exposures as may occur in homes or at work. Until there is evidence to the contrary, it will be prudent to minimize such exposures through a variety of practical and economical measures. This book is one resource for such efforts.

The book starts with the problem definition. The indoor air pollutant sources, their exposure potential and the rated health effects are presented for specific (asbestos, radon and formaldehyde) and a family of (combustion generated, volatile organic compounds, pesticides, and biogenic particles) pollutants. This is followed by proactive source control of inorganic, organic, and biogenic contaminants. The pollution control strategy then shifts to the reactive means of ventilation and air cleaning. The author then deals with the difficult issue of indoor air quality policy and regulatory considerations. Also suggested are regulatory and nonregulatory strategies to achieve the desired end result. These portions of the book serve as an excellent source of handy reference material. The unique feature of this book is in its two concluding chapters. They are dedicated to practical diagnosis and problem solving of air quality, both in residences and public access buildings. The book also has copious references at the end of each chapter (677 references total).

This is an excellent reference, practical troubleshooting and problem–solving book. It is a timely addition to the field of indoor air quality. It is an invaluable resource not only for professionals in health care, industry, construction, government, and academia, but also for every concerned citizen who cares about the family's well-being and the quality of air they breathe.

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The Arthur Young Guide to Water and Wastewater Finance, by George A. Raftelis, Lewis Publishers, Chelsea, MI 48118 (1989), 220 pages, U.S. List Price: $49.95

This book provides the reader with principles and guidelines for financial planning and rate setting techniques that relate to the water and wastewater utilities business. The book is organized into two primary sections dealing with financing and pricing of water and wastewater services. Many traditional and innovative financing methods and pricing structures are also included. The author has extensive background in this field which has resulted in many practical and useful guidelines that are well-suited for anyone involved with the financing and pricing of water and wastewater utilities.

This book is ideally suited for managers of utilities that are involved in financial strategies to build, own, or operate water treatment facilities.

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Health Effects of Drinking Water Treatment Technologies, Drinking Water Health Effects Task Force, Lewis Publishers, Inc., Chelsea, MI 48118 (1989), 145 pages, U.S. List Price: $37.50

This book evaluates the risks and benefits of drinking water treatment technologies. An assessment and comparison is made of the chemicals used in treatment, the by-products of chemical treatment, and the nontreatment of drinking water.

The EPA and the task force that prepared this book are generally recognized experts in the field of drinking water treatment technology and toxicology.

This book is an excellent documentation of the state-of-the-art of water treatment and associated toxicology. It is the best, most complete, single source document in this important field. It should be useful to water treatment planners, engineers, operators, and management as an authoritative reference.

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Hazardous Waste Reduction in the Metal Finishing Industry, PRC Environmental Management, Inc., Noyes Data Corporation, Park Ridge, NJ (1989), 205 pages [ISBN No.: 0-8155-1223-6] U.S. List Price: $42.00

The metal finishing industry in the United States is responsible for the generation of a variety of hazardous waste streams. This book provides the results of hazardous waste reduction audits performed at three medium-sized plants operating their own waste-water treatment facilities in California (15 to 35 employees, between 10,000 to 30,000 ft^2 of plant space, and wastewater generation of 10,000 to 30,000 gallons per day). The objective of the study was to identify waste reduction opportunities in the metal finishing industry and to develop an audit protocol for metal finishers to evaluate the waste reduction opportunities applicable to their specific operations.

The organization of the book is therefore not surprising. The first chapter reports on the summary and conclusions listing waste reduction options and the identified need for a waste reduction program among the various plants. A notable component of their recommendations in Chapter 2 is the audit protocol which is detailed in Chapter 8. The rest of the chapters detail waste reduction options and alternatives (none of which appear to be unusual or innovative), and their findings at the three plants.

Appendix D which provides a detailed waste reduction audit checklist is probably the most notable feature of the book and could be quite useful to metal finishers who would like to examine their waste reduction options in a systematic manner.

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Fermentation Process Development of Industrial Organisms, by Justin O. Neway, Marcel Dekker, Inc., New York, NY (1989), 324 pages [ISBN No.: 0-8247-7917-7] U.S. List Price: $99.75

Commercial fermentation processes have been operated by humans for many centuries, and the variety of fermentation products has increased from foods and beverages to healthcare products and industrial chemicals that are essential to our civilization. Recent developments in recombinant DNA and mammalian cell technologies have opened tremendous opportunities in fermentation processes, while, on the other hand, presenting challenging problems in process development. Due to improvements in our understanding of the biology of organisms and the ability to control the metabolic pathways involved, modern fermentation process development includes an increasingly higher degree of physiological control. This book presents methods of manipulating the physiology and biochemistry of organisms to economically produce large quantities of industrial products of the appropriate quality. It covers both biological and engineering aspects of process development, and the interactions of the two are emphasized.

The book contains six chapters, each describing development of fermentation processes based on a particular organism. Three types of bacteria (actinomycetes, bacilli, and coryneform bacteria), yeast, fungi, and mammalian cells are included. Contents of each chapter include the use of mutation and genetic engineering for strain development, aspects of medium development, and scale-up of the processes. Practical yet important considerations in commerical processes, such as fermentation product quality and harvestability and regulatory compliance, are discussed. Extensive coverages are provided in the engineering aspects of actinomycete fermentation scale-up, extracellular enzymes and insecticides production by bacilli, amino acids production by coryneform bacteria and laboratory- to production-scale culture systems for mammalian cells. Each chapter illustrates the diversity of industrial fermentation processes and describes aspects of process development that are specific to the particular organism of that chapter. There are also abundant materials covering process development methodologies that can be applied to fermentation processes in general, including processes based on other organisms.

This book provides valuable information for industrial microbiologists, biotechnologists, geneticists, biochemists, and bioprocess engineers who are involved with the development of industrial–scale biological processes.

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An Indoor Air Quality Model

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Since the early 1980s, questions related to indoor air quality have often been faced by environmental professionals. Investigations of indoor air problems involve monitoring, source determination and/or prediction of air quality. Dr. Leslie E. Sparks of Air and Energy Engineering Research Laboratory of the United States Environmental Protection Agency, Research Triangle Park, NC has developed an Indoor Air Quality (IAQ) model [*1*]. The estimate of the impact of various pollutant sources on indoor air quality can be obtained using this model. The model is available for public use.

A copy of the IAQ model along with a user manual was obtained from Dr. Sparks. A 5 1/4″ double sided, double density diskette can accommodate all 12 files of the model. It can be run on an IBM-PC, XT, AT or compatible. The use of a color graphics adapter (CGA) or an enhanced graphics adapter (EGA) is suggested in the manual for obtaining the graphs.

The accompanying manual is divided in six sections. Section 1 reviews the IAQ model and the procedure to start the program. The theory behind the model and the solution techniques are explained in section 2. A user guide for the model with two examples is given in section 3. Seven case studies are documented in section 4. The model has been applied to a test house in section 5. The last section gives hints on using the model.

Typing "INDOOR" at the DOS prompt and pressing the ENTER/RETURN key takes the user into the model. Simple and self explanatory menus and submenus make data entry much easier for the user. Moreover, the menu-driven data-input and the graphics-output user interfaces make data entry and analysis of results very quick. The use of the program does not require any special computing skills or knowledge on the user's side. The only point which needs to be mentioned is data entry in the "Interconnections" submenu, while defining rooms under the "Data Input" menu. The air flow entering and/or leaving different rooms should be entered carefully. A non-zero figure for the net balance indicates an error which requires checking various air flows, and re-entering the correct figure. Once the data are entered correctly, output can be obtained by running the model. The output is displayed on the screen or a hard copy can be printed, depending upon the selection made at the output menu. The results can also be stored in a separate file for each case.

In order to test the model, different examples and case studies given in the manual [*1*] were tried initially. These cases are:

1) estimation of NO_x concentration in a room due to usage of a kerosene heater,

2) estimation of CO_2 concentration in various rooms of a building due to usage of a kerosene heater, and

3) determination of particulate loading as a result of cigarette smoking in an office building.

Various situations for the case (3) of cigarette smoking were tried. For example: continuous or fixed cigarette source, random cigarette source and the use of a filter. Though the results obtained were comparable to those given in the manual, plots of time versus concentration could not be printed. With an EGA, very good plots were obtained on screen, with a curve of different color for each room, but even the "PRINT SCREEN" command was not able to print it on either an IBM proprinter or a Panasonic printer.

To check the applicability of the model to the problems given in open literature, a problem from the book "Indoor Air Pollution" by Wadden and Scheff [2] was tried. The problem given in Chapter 9 is on the determination of indoor pollutant concentrations inside a restaurant kitchen due to combustion sources. The source estimation procedure of the IAQ model is not flexible enough to handle a variety of sources contributing to indoor air levels. It was not possible to define these sources under the "other sources" option in the "Define Rooms" submenu because the IAQ model does not allow periodic usage of sources in this option. Moreover, the model could be run for estimating NO_x concentrations and not NO or NO_2 as required by the problem.

Some of the observations we made during the review of this model are listed below:

1) The model can run only for one pollutant at a time. If one needs to know concentrations of two or more pollutants for a room or a building, then the model requires rerunning for each pollutant.

2) The model has predefined pollutant sources. Other sources can be defined only if they are used continuously.

3) Cigarette smoking can be defined for continuous usage only. If the situation demands for periodic turning ON and OFF at the source, this variation is not possible except in the case of a kerosene heater and an unvented stove. This limitation forces the user to simulate the case for some other source.

Overall, the IAQ model is efficient for quick turnaround and gives quite satisfactory results for houses, small office buildings and commercial establishments. A much–sought modified version could make it more useful and could be applied for even larger buildings with more rooms.

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1. Sparks, L. E., Indoor Air Quality Model Version 1.0, EPA-600/8-88-097a, U.S. Environmental Protection Agency, Research Triangle Park, NC, September 1988.
2. Wadden, R. A. and P. A. Scheff, *Indoor Air Quality*, John Wiley & Sons, New York, NY (1983).

Waste Minimization in a Leading Ethical Pharmaceutical Company

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In the pharmaceutical industry, waste disposal can constitute an appreciable fraction of the cost of bulk drug manufacture. Waste minimization is not new to Merck or to the pharmaceutical industry. At Merck, it was realized several years ago that it made good technical and business sense to continually emphasize efforts to eliminate or at least reduce waste generation whenever possible. Examples of the successful incorporation of waste minimization practices during bulk drug manufacture as well as during research and development follow.

An example of the successful incorporation of waste minimization practices early in the process development cycle occurred during the development of a new broad spectrum antibiotic unparalleled in its effectiveness. Between the initial development of the process in our Research Laboratories, through scale-up in our Pilot Plant and full-scale manufacture of this product—a period of about five years—Merck engineers were able to devise and implement waste minimization techniques to eliminate half of the waste that would have otherwise been generated from this multi-step synthesis process. Although environmental considerations provided the initial driving force for waste reduction, waste minimization did not end with the introduction of the product into full scale manufacturing. Over the five years this product has been in production, several process modifications have been implemented, which have dramatically reduced waste loads. For example, methylene chloride usage has been reduced by 82%, resulting in an annual savings in excess of one million dollars. This was accomplished through process changes to eliminate materials that made recovery of the methylene chloride impractical, modifying the process to use recovered material and development of improved recovery techniques.

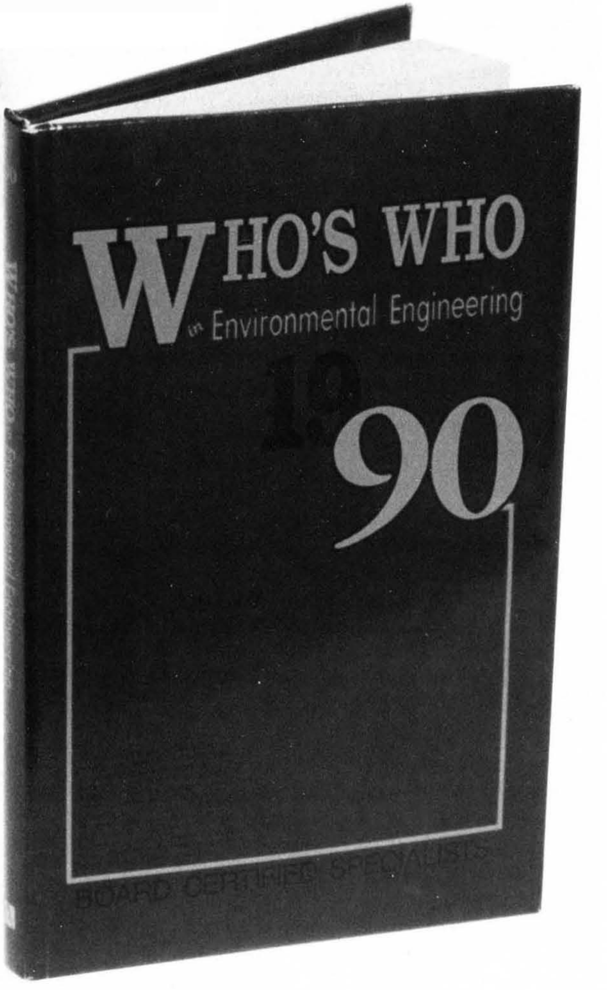
In another step of this process, solvent distillation and internal recovery of an acetone-water mixture reduced annual usage of acetone by 80% which resulted in an annual savings of 1.3 million dollars. Yet another example of waste reduction involved isoamyl alcohol, recovered for reuse in this process. At plant start-up, the technology to recover it from the waste stream for reuse had not yet been developed. The entire waste stream was stored while development engineers devised a scheme to recover the inventoried waste as well as that generated daily. This resulted in an annual savings of 1.4 million dollars. This manufacturing process is still undergoing modification to totally eliminate methylene chloride from the process, and there has been significant progress on this front.

Another successful example of waste minimization is in the manufacture of a newly introduced cholesterol-lowering drug. The first generation process utilized toluene to extract the active ingredient from the biomass which generated spent solids and mother liquors rich in toluene to be disposed of. A second generation process in which toluene was replaced with an environmentally more acceptable solvent, isopropyl acetate, was quickly developed. When production was switched to the second generation process, technology for recovering isopropyl acetate from the waste stream had not been developed and consequently the waste was incinerated off-site. Subsequently, a recovery scheme was developed, put into practice, and isopropyl acetate is currently being recovered (>90%). The economic and environmental advantages of this solvent switch are substantial.

In the downstream processing of the drug, methanol is used. Initially, the spent methanol-water mixture was discharged to an activated sludge treatment plant. Presently, due to loading restrictions, the methanol-water mixture is sent off site for recovery and non-process reuse by others. Overall, a savings of \$350,000/yr. has been realized. In the purification step, ethyl acetate is used. During initial production, a recovery scheme had not been developed and hence the spent solvent was shipped off site for recovery. Subsequently, a recovery scheme was developed and presently the solvent is recovered (90%) on-site and reused, resulting in a savings of \$370,000/yr.

Over the past three years, waste minimization efforts have increasingly been brought to bear in the early stages of the product development cycle. Waste minimization is definitely a 'process–related opportunity' and is a major objective of the R&D program. In fact, waste minimization is a full–fledged element of process development. Recently, we have begun to use a novel expert–system–based Environmental Assessment System (EASY), conceived, designed and implemented by Merck scientists, to assess potential environmental impact and implications of manufacturing processes during the early stages of development. EASY can currently handle the disposition of liquid, gas or solid phase wastes. The system looks for solvent recovery opportunities, preferred ways of handling toxic, hazardous, biocidal and malodorous chemicals. To achieve this, the system uses a comprehensive environmental data base developed in-house. In addition, EASY also predicts the fate of the waste stream components in a typical activated sludge treatment plant. It uses a "treatability index" to predict effluent toxicity, oxygen demand of the effluent, stripping of VOCs, sludge production and sludge toxicity. The assessment is based on a waste stream summary generated by a computer–aided process evaluation (PROVAL™) package, also developed in-house. EASY provides a systematic way of evaluating process concepts for their potential environmental impact and assists with the goal of developing processes with very low environmental profiles. EASY has been validated in an expert system environment by applying the concept to a number of development projects.

In practice, once a process has undergone significant development at the Pilot Plant scale, it is generally difficult and costly to make major changes and modifications. Also, regulatory constraints that apply to the pharmaceutical industry restrict modification of a process once clinical efficacy of the drug is established. For these reasons, the waste reduction approach at Merck & Co., Inc. emphasizes integral, front-end changes rather than relying solely on end-of-pipe treatment techniques.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Bench–Scale Evaluation of Calcium Sorbents for Acid Gas Emission Control

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Calcium sorbents for acid gas emission control were evaluated for effectiveness in removing SO_2/HCl and SO_2/NO from simulated incinerator and boiler flue gases. All tests were conducted in a bench-scale reactor (fixed-bed) simulating fabric filter conditions in an acid gas removal process. Reagent grade $Ca(OH)_2$ was used to establish baseline sorbent performance. The reactivity of reagent grade $Ca(OH)_2$ with HCl from SO_2/HCl mixtures gradually increased with decreasing approach to saturation temperature. SO_2 reactivity toward $Ca(OH)_2$ was very sensitive to approach to saturation. Novel calcium silicate sorbents were tested for reactivity with both SO_2 and HCl. A "thermal window" for optimum NO removal was found at 90°C (194°F) when $Ca(OH)_2$ was used at SO_2/NO ratios of 1:1. Reactivity of $Ca(OH)_2$ toward SO_2 from SO_2/NO mixtures was very sensitive to approach to saturation, while reactivity with NO was insensitive. Several additives were subsequently tested to determine optimum sorbent combinations for SO_2/NO control. To date the most promising additives are $Mg(OH)_2$ and Na_2HPO_4 at 10 mol percent concentrations. As with SO_2/HCl, calcium silicate has been shown to be superior for SO_2/NO capture. Some implications for larger-scale process configurations and sorbent selection for HCl/SO_2/NO control are discussed. Future activities and limited larger–scale pilot plant results are also discussed.

INTRODUCTION

The widespread recognition of municipal solid waste incineration (MSWI) as a means of disposing of refuse prompted the interest in the control of acid gas emissions into the atmosphere. Both wet and dry processes are considered for the removal of acid gases such as HCl, SO_2, and NO. Wet scrubbers (with preceding ESP) are particularly favored for trace heavy metal control in addition to acid gas control [*1*]. Wet scrubbers can achieve 95 percent removal of HCl and 90 percent removal of SO_2 and can be designed for NO_x control [8]. However, they are costly and technically complex compared to dry systems. Spray drying, using a fabric filter for particulate collection, is particularly widespread.

In this process, dry powdered sorbent is injected into the duct containing flue gas that is humidified to decrease the approach to saturation temperature. The concentration of acid gases is reduced by chemical reaction occurring during evaporative cooling—achieved by the evaporation of a finely atomized $Ca(OH)_2$ slurry into hot flue gas. Compared with spray drying, dry sorbent injection into the duct offers the possibility of an even more economical process for the cleanup of MSWI flue gas.

The approach to saturation is known to be a very important parameter governing the reactivity of sorbent during dry sorbent duct injection. Since the dry injection offers only limited sorbent utilization, a fabric filter is commonly used as a particulate collector to allow for additional reaction of acid gas with sorbent deposited on the surface of the filter. Effective acid gas control could be achieved in such a way as in tests previously conducted by Environment Canada [*10*]. Post–combustion control of NO_x is generally perceived as the most costly of the three acid gases mentioned above.

The objective of this study was to investigate at the bench–scale the feasibility of dry injection processes for the removal of HCl, SO_2, and NO. A fixed–bed reactor was used to evaluate potential calcitic sorbents for the control of acid gas emissions. The approach to saturation between 10°C and 40°C (18°F and 72°F) was investigated, being representative of operational conditions encountered during the duct injection process. Based on the findings of the bench-scale experiments as well as on limited pilot–scale results discussed here, some recommendations were given concerning the operation of dry sorbent injection systems for acid gas emission control.

EXPERIMENTAL

Apparatus

The core of the experimental apparatus, shown in Figure 1, was the sand–bed reactor, where the test gas with the desired SO_2/HCl or SO_2/NO concentration reacted with the alkaline sorbent. This type of reactor has been successfully used in past screening of sorbents for SO_2 removal [4], [5]. A similar type of fixed–bed reactor system was employed for the study of adsorption of HCl on solid slaked lime [6].

The reactor was a vertical packed bed of 1 g sorbent dispersed in 40 g of inert silica sand. The entire bed was supported on a 45 mm diameter fritted glass plate in a glass cylinder. The simulated flue gas passed down through the sand-bed at a face velocity of 6 cm/s. Commercially available calibrated span gases of SO_2 in nitrogen or NO in nitrogen were used as the test gases. The desired concentration of HCl in the flue gas was obtained by mixing pure HCl with the span gas stream.

For SO_2/HCl removal testing, 500 ppm SO_2 and 1,000 ppm HCl concentrations were used; whereas, for SO_2/NO, nominal concentrations were 400 ppm of both SO_2 and NO. The SO_2/NO gas stream also contained 5 percent by volume of O_2 obtained by mixing SO_2 and NO span gases with air. The nitrogen purging system was incorporated to address the problems associated with the high water affinity of HCl and the resulting corrosion risks.

Two electrically heated reactor systems were used interchangeably during testing. The operating temperature range was 54°C-177°C (130°F-350°F) for SO_2/HCl testing. Initial baseline testing of SO_2/NO removal was done in the electrically heated reactor. Following sorbent screening, SO_2/NO was removed in the reactor heated by the water bath operated at 90°C (194°F).

In order to test the effect of moisture in the flue gas, water was continuously injected into the evaporation chamber by a syringe type dispensing pump, equipped with two syringes to allow continuous operation with a transient-free switchover period. Steady evaporation was achieved in an electrically heated sand reservoir, from which water vapor was injected into the process gas. The moisture was removed from the gas by the condenser/ice–cooled trap and analyzed for chloride contents. The SO_2 and NO concentration in the outlet gas was continuously monitored by Thermoelectron Model 40 pulsed fluorescence analyzer and Thermoelectron Model 10A chemiluminescence analyzer working in NO_x mode, respectively. A 1 h period was arbitrarily selected for an experimental run as being representative of a typical fabric-filter cleaning cycle.

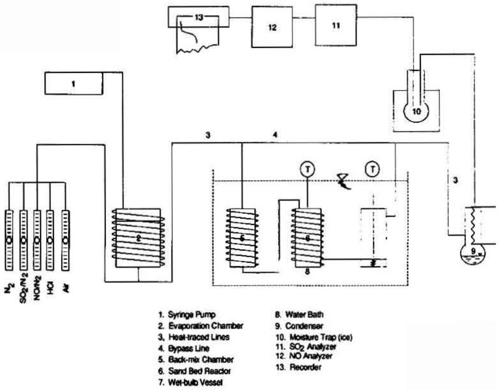

Figure 1. Experimental apparatus.

Analytical Procedures

The removal of SO_2 and NO was determined by integration of the 1 h concentration curve recorded by the analyzer. The removal of HCl by the sorbent in the sand-bed reactor was determined by washing the bed and analyzing the filtrate by ion chromatography for chloride. After completing the run, the reactor was cooled and the sorbent containing sand was removed to a beaker. The reactor was washed with distilled water, and the rinse, together with an additional amount of water, was poured into the beaker containing sand. The contents of the beaker were stirred at room temperature for 1 h. The sample was filtered, diluted, and analyzed by ion chromatography. The amount of chloride in the reactor wash and in the condensate was compared against the amount of HCl injected into the span gas, as shown by a flowmeter. The mass balance of HCl could usually be closed to within ± 10 percent. The reactivity of sorbent is described here as the ratio of millimoles of acid-gas pollutant removed after 1 h contacting in the sand-bed reactor per 100 millimoles of $Ca(OH)_2$.

Sorbents

Reagent grade $Ca(OH)_2$ (Fisher C-97) was selected to establish the baseline reactivity of lime with HCl, SO_2, and NO. The B.E.T. specific surface area measured by nitrogen adsorption was 12.4 m^2/g for this sorbent. Several additives were tested to promote the removal of NO from SO_2/NO gas. Also tested were novel silicate sorbents, described earlier as being capable of superior reactivity with SO_2 compared to dry hydrated lime when contacted under dry sorbent duct injection conditions [5]. These sorbents were produced by slurrying flyash and $Ca(OH)_2$, in ratios varying from 3:1 to 10:1 at 90°C (194°F) for 8h. The above conditions were shown to produce sorbents having significantly higher B.E.T. specific surface areas and up to about 3 times the reactivity of reagent grade $Ca(OH)_2$ with SO_2 [5].

RESULTS AND DISCUSSION

Reactivity with SO_2 and HCl

The first series of bench-scale experiments were directed toward establishing the baseline reactivity of reagent grade $Ca(OH)_2$ as a function of the approach to saturation temperature (relative humidity) in the reactor. The removal of HCl from HCl/N_2 gas was tested first: the results are shown in Figure 2. For these tests the HCl concentration was 1,000 ppm and the absolute humidity was constant at 0.1g H_2O/g of dry gas; the temperature of the gas varied from 66 to 177°C (150 to 350°F). Relative humidity (controlled by temperature) had a positive effect on the reactivity of reagent grade lime with HCl, with reactivity increasing with the increasing relative humidity in the reactor (decreasing approach to the adiabatic saturation temperature). Under the experimental conditions (1 g of $Ca(OH)_2$ and 1,000 ppm HCl), the reactivity of 90 mmols HCl/100 mmols $Ca(OH)_2$ would correspond to 100 percent removal of HCl from the simulated flue gas. Based on these experimental results, 30°C (54°F) approach to saturation or less would be recommended to achieve at least 80 percent removal of HCl from the flue gas.

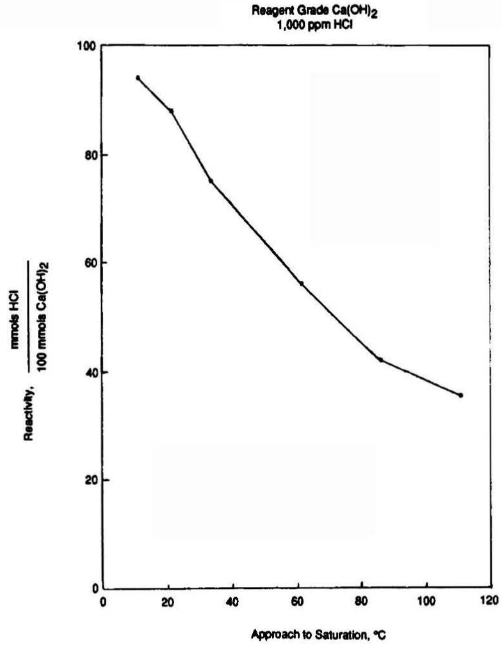

Figure 2. The effect of the approach to saturation on reactivity of $Ca(OH)_2$ with HCl.

Because typical MSWI flue gas would contain SO_2 in addition to HCl, several tests were performed to evaluate the effect of the approach to saturation (relative humidity) on the reactivity of reagent grade lime with SO_2 alone. The results are presented in Figure 3. The approach to saturation was affected by varying the temperature from 66°C to 177°C (150°F to 350°F). Two reaction regimes could be defined based on findings presented in Figure 3. For the approach to saturation greater than about 35°C (63°F), reactivity with SO_2 was low, revealed little sensitivity toward relative humidity, and ranged from 4.9 to 6.2 mmol SO_2/100 mmol $Ca(OH)_2$. The reactivity was very sensitive toward relative humidity for the approach to saturation of less than 35°C (63°F) and was increasing with the decreasing approach to saturation temperature, to reach an experimental maximum of 17 mmol SO_2/100 mmol $Ca(OH)_2$ at 10°C (18°F) approach.

For the conditions used in the above experiments, 35°C (63°F) approach would correspond to about 18 percent relative humidity. According to data on equilibrium water vapor adsorption, about 1.2 molecular layers of water would adsorb on lime at 18 percent relative humidity [7]. Results of this study agree quite well, therefore, with others indicating that significant SO_2 capture by dry $Ca(OH)_2$ requires at least a 1.0 molecular layer of adsorbed water on lime surfaces [9].

The reactivity of reagent grade $Ca(OH)_2$ with combined SO_2/HCl was also tested in the sand-bed reactor. The results of experiments when 1,000 ppm HCl and 500 ppm SO_2 were simultaneously present in the flue gas are shown in Figure 4. For comparison, the results for HCl or SO_2 alone are presented with broken lines in Figure 4. As was the case when only one acid gas was present in the flue gas, sorbent reactivity when HCl and SO_2 were present increased with decreasing approach to adiabatic saturation. The reactivity with HCl absorbed from flue gas containing HCl and SO_2 was essentially unchanged, compared to reactivity with HCl alone. The reactivity with SO_2 was somewhat enhanced by the simultaneous presence of HCl in the flue gas for approach to saturation of less than 60°C (108°F).

It is possible that the deliquescent product of the $Ca(OH)_2$/HCl reaction might have subsequently promoted reactivity of $Ca(OH)_2$ with SO_2. For the conditions tested, it appears that the reactivity of lime with HCl is about one order of magnitude higher than that with SO_2.

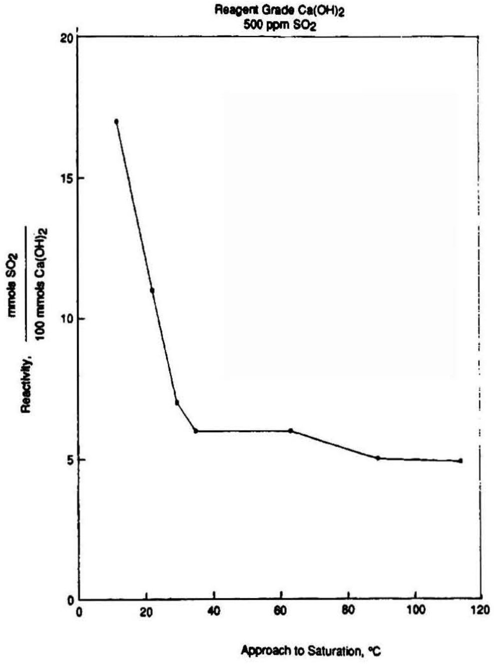

Figure 3. The effect of the approach to saturation on reactivity of $Ca(OH)_2$ with SO_2.

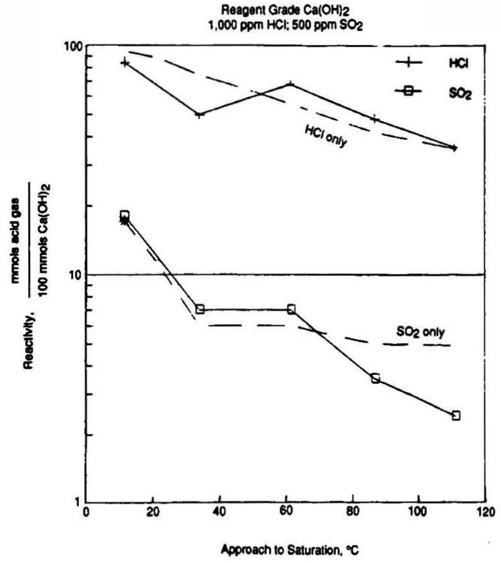

Figure 4. The effect of the approach to saturation on combined reactivity of $Ca(OH)_2$ with SO_2 and HCl.

The reactivity with HCl was significantly less sensitive to the approach to saturation than with SO_2. For example, decreasing the approach to saturation from 35°C to 12°C (63°F to 22°F) increased the reactivity with HCl by 33 percent from 60 to 80 mmols HCl/100 mmol $Ca(OH)_2$. The same change increased the reactivity with SO_2 by 183 percent from 7 to 17 mmols SO_2/100 mmols $Ca(OH)_2$.

Previous work [5] has demonstrated that silica–enhanced $Ca(OH)_2$ was significantly more reactive toward SO_2 than $Ca(OH)_2$ alone. For fixed sorbent preparation conditions (90°C for 8h), the reactivity increased with the increasing weight ratio of flyash to lime [5]. Sorbents were prepared for this study using reagent grade $Ca(OH)_2$ and low calcium flyash from the Clinch River Plant in Carbo, VA. Tested weight ratios of flyash to $Ca(OH)_2$ were 10:1, 5:1, and 3:1, and the approach to saturation was varied from 20°C to 40°C (36°F to 72°F). The results are presented in Figure 5, which gives the reactivity of silica-enhanced sorbents as a function of the approach to saturation. Baseline results for reagent grade $Ca(OH)_2$ exposed to 1,000 ppm HCl and 500 ppm SO_2 are shown by the broken lines.

Only moderate enhancement of reactivity was observed with a flyash–to–$Ca(OH)_2$ weight ratio of 10:1. No enhancement was measured for the 5:1 sorbent, and 3:1 sorbent revealed lower reactivity than reagent grade $Ca(OH)_2$. This is in contrast to earlier findings about the reactivity of silica-enhanced sorbents for removal of SO_2 alone [5]. Apparently, the reaction product with HCl blinds the surface and precludes active sites from reacting with SO_2.

One way that blinding might have occurred was the combination of the surface moisture of the silicate sorbent with $CaCl_2$ reaction product. Bound moisture would probably not be available for the reaction with SO_2. The ability of silicate sorbent to release surface moisture to make it available during the reaction of $Ca(OH)_2$ with SO_2 is believed (aside from its high specific surface area) to be the reason for its greatly enhanced reactivity with SO_2 compared to $Ca(OH)_2$. Silica–enhanced sorbents captured more HCl per unit mass of $Ca(OH)_2$ than did reagent grade $Ca(OH)_2$. For example, at 40°C (72°F) approach to saturation, the reactivity of reagent grade $Ca(OH)_2$ was about 70 mmols HCl/100 mmols $Ca(OH)_2$ when exposed to 1,000 ppm HCl and 500 ppm SO_2. Silica–enhanced sorbents revealed an average reactivity of about 110 mmols HCl/100 mmols $Ca(OH)_2$ after exposure to acid gas pollutants at the same conditions in the sand–bed reactor. There was little dependence of calcium silicate reactivity with HCl on the flyash–to–$Ca(OH)_2$ weight ratio. Reactivity varied from 107 to 112 mmols HCl/100 mmols $Ca(OH)_2$ for the 10:1 to 3:1 weight ratio range and 40°C (72°F) approach to saturation. For the same conditions, the reactivity with SO_2 varied from 4.6 to 9.5 mmols SO_2/100 mmols $Ca(OH)_2$ for the flyash-to-$Ca(OH)_2$ weight ratio range from 3:1 to 10:1.

Reactivity with SO_2 and NO

Because NO is a major acid gas pollutant in MSWI flue gas, effort was directed to investigate potential sorbents for its removal under duct injection conditions. As in the approach discussed earlier for testing the reactivity of sorbents with HCl and SO_2, reagent grade $Ca(OH)_2$ was tested first. Temperature in the reactor was varied from 70°C to 180°C (158°F to 356°F), and absolute humidity was constant at 0.1g H_2O/g dry gas. The concentration of NO was 400 ppm, and the ratio of SO_2 to NO—known to affect the removal of NO from the flue gas [2]—was 1:1.

The simulated flue gas contained 5 volume percent of oxygen (initial experiments indicated no removal of NO without oxygen present in the flue gas). The results are shown in Figure 6, giving the reactivity as a function of the temperature/approach to saturation in the reactor. The highest reactivity of 0.8 mmol NO/100 mmol $Ca(OH)_2$ was achieved at 177°C (350°F). However, with these conditions of temperature/relative humidity, only low reactivity with SO_2(5 mmols SO_2/100 mmols $Ca(OH)_2$) would be expected for simultaneous removal of SO_2/NO. The temperature of 90°C (194°F), for which somewhat higher reactivity with SO_2 was measured, seems, therefore, to be the optimum for the simultaneous removal of SO_2/NO, based on the available data presented in Figure 6. This temperature agrees with the previously reported so-called thermal window within 87°C to 107°C (189°F to 225°F) where SO_2 and NO can react simultaneously [3].

Also shown in Figure 6 is the reactivity of $Ca(OH)_2$ with SO_2 for simultaneous removal of SO_2 and NO. It was

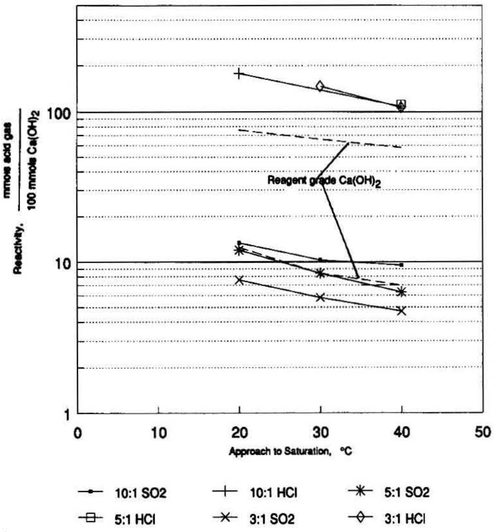

Figure 5. The reactivity of silica-enhanced sorbents with SO_2 and HCl.

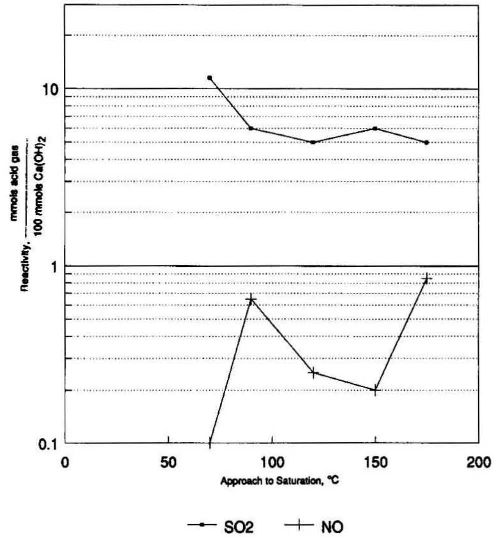

Figure 6. The temperature dependence of $Ca(OH)_2$ reactivity with SO_2 and NO.

a strong function of the approach to saturation (relative humidity) in the reactor, with reactivity increasing significantly for the approach to saturation less than 35°C (63°F) (relative humidity greater than 18 percent). The reactivity of $Ca(OH)_2$ with NO was not a clear function of the approach to saturation. However, it has been reported [2], [3] that moisture in the flue gas is necessary for NO removal.

Another factor that has been recognized as affecting the reactivity of calcitic sorbents with NO is the SO_2/NO ratio. This has been confirmed during this study. When a mixture of NO/N_2 and 5 percent oxygen was contacted with $Ca(OH)_2$, only 0.12 mmol NO/100 mmol $Ca(OH)_2$ reactivity was measured at 90°C 35°C (63°F) approach to saturation. The reactivity was 0.65 mmol NO/100 mmol $Ca(OH)_2$ for SO_2/NO ratio of 1:1, with other parameters unaffected. The comparison of data presented in Figure 6 with those discussed in Figure 4 indicates that the reactivity of calcitic sorbents with acid gases follows the descending order $HCl > SO_2 > NO$. $Ca(OH)_2$ was measured to be about one order of magnitude less reactive with NO than it was with SO_2.

In the next step, several additives were tested with the goal of enhancing reactivity of $Ca(OH)_2$ with NO. Each additive was used at the 10 mol percent concentration level induced by slurrying $Ca(OH)_2$ with a given additive for 10 min and oven drying the resulting 50 percent solids slurry overnight. The conditions in the sand–bed reactor were 400 ppm SO_2, 400 ppm NO, 90°C (194°F) temperature, and 35°C (63°F) approach to saturation. The results are shown in Figure 7. The most promising additives selected so far were $Mg(OH)_2$ and $NaHPO_4$. A certain increase of reactivity with SO_2 was also observed for these two additives. More bench–scale and pilot–scale testing are needed to fully evaluate the effectiveness of additives on reactivity of $Ca(OH)_2$ with NO.

Another sorbent tested for simultaneous removal of SO_2 and NO was silicate. It has been demonstrated that silicate sorbents are more reactive toward NO than reagent grade $Ca(OH)_2$ when prepared with 10 mol percent NaOH [2]. The sorbents were prepared with flyash–to–$Ca(OH)_2$ weight ratios of 10:1 and 3:1. Both had 10 mol percent NaOH added [based on $Ca(OH)_2$] and were slurried at 90°C (194°F) for 8h. The results of testing are presented in Figure 8 for approaches to saturation ranging from 10°C to 30°C (18°F to 54°F) and 400 ppm NO with a SO_2/NO ratio of 1:1. For a given approach to saturation, the reactivity with both SO_2 and NO was increased with increasing flyash–to–$Ca(OH)_2$ weight ratio of the sorbent. Similar to baseline results discussed earlier, reactivity with NO for any given sorbent increased, and reactivity with SO_2 decreased for the increasing approach to saturation. At 30°C (54°F) approach to saturation, the reactivity of sorbent prepared by slurrying flyash with $Ca(OH)_2$ at a 3:1 weight ratio was significantly higher for both SO_2 and NO than the reactivity measured for the reagent grade $Ca(OH)_2$.

On the commercial scale, silicate sorbents with high flyash–to–$Ca(OH)_2$ weight ratio would be achieved by increasing the recycle of flyash and spent sorbent. Calcium sulfite ($CaSO_3$) would also be present when recycling spent sorbent. Several experiments were performed to evaluate the effect of $CaSO_3$ alone on the reactivity of $Ca(OH)_2$ with NO. When $CaSO_3$ was slurried with $Ca(OH)_2$ at a 4:1 weight ratio (no flyash), oven dried, and exposed to 400 ppm NO/400 ppm SO_2, flue gas in the sand–bed reactor operated at 35°C (63°F) approach to saturation, the reactivity was 1.52 mmol NO/100 mmol $Ca(OH)_2$ and 12.41 mmol SO_2/100 mmol $Ca(OH)_2$ (compared to 0.65 mmol NO and 6.0 mmol SO_2/100 mmol $Ca(OH)_2$ for reagent grade).

Reactivity of only 1.09 mmol NO/100 mmol $Ca(OH)_2$ was measured when the same sorbent was exposed to gas containing only 400 ppm NO (no SO_2). It seems, therefore, that there is some other effect besides formation of $CaSO_3$ on the surface of $Ca(OH)_2$ prior to reactivity with NO. Possibly some catalytic effect of the combined presence of SO_2 and O_2 facilitates oxidation of NO. To better simulate commercial systems flyash, $Ca(OH)_2$, and $CaSO_3$ were slurried at a 4:1:4 weight ratio, with 0.1 mole NaOH per mole $Ca(OH)_2$ added. The resulting reactivity of this sorbent with NO increased to 2.21 mmol NO/100 mmol $Ca(OH)_2$. Ultimately, 10 mol percent of $Mg(OH)_2$ was added to the above flyash/$Ca(OH)_2$/$CaSO_3$/NaOH sorbent, and the reactivity with NO was 2.71 mmol NO/100 mmol $Ca(OH)_2$.

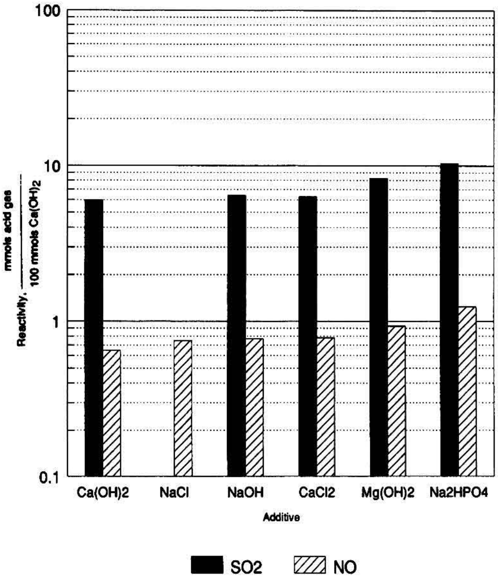

Figure 7. Screening of additives for the enhancement of $Ca(OH)_2$ reactivity with SO_2 and NO.

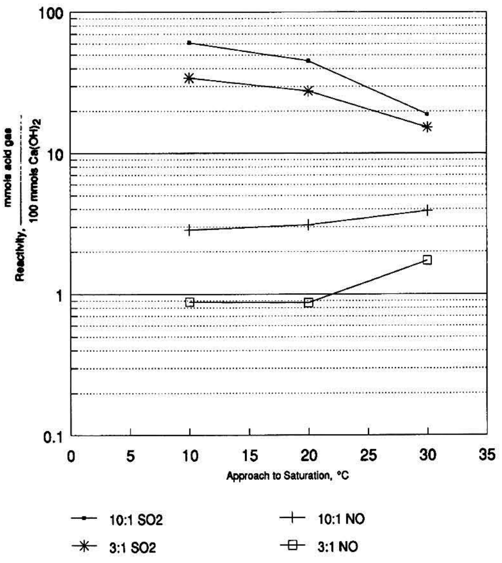

Figure 8. The reactivity of silica–enhanced sorbents with SO_2 and NO.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations are based on the results of this study.

- The reactivity of calcitic sorbents with the three acid gases investigated during this work could be arranged in decreasing order as HCl > SO_2 > NO. The reactivity with NO would be about 2 orders of magnitude lower than with HCl.
- SO_2 should be removed from the SO_2/HCl or SO_2/HCl/NO flue gas at an approach to saturation of 35°C (63°F) or lower to ensure the buildup of at least 1.0 monolayer of molecular water on the surface of the sorbent (relative humidity of about 20 percent).
- High reactivities can be achieved with HCl for almost all conditions tested, and this pollutant should be the easiest to remove of the three tested.
- Low removals of NO were measured across the sand-bed reactor (generally below 10 percent). The reactivity with NO was not proportional to the relative humidity in the reactor. Optimum temperature for the removal of NO was found to be 90°C (194°F).
- Calcium silicate sorbents were more reactive than dry hydrated lime for the removal of acid gas pollutants. The greatest enhancement was observed for reactivity with SO_2 and NO. Severe blinding of active sites, combined with blinding of surface moisture normally available for the reaction, occurred as a result of reaction with HCl.
- Silicate sorbents were more reactive with HCl than reagent grade $Ca(OH)_2$. However, the enhancement of reactivity with SO_2 (simultaneous HCl/SO_2 removal) was measured only for flyash-to-$Ca(OH)_2$ weight ratio of 10:1.
- Several additives were evaluated for the enhancement of reactivity with NO. The two most promising were $Mg(OH)_2$ and Na_2HPO_4. The former seems to be more attractive commercially because of its lower price and the potential for using dolomitic lime for calcium silicate preparation. More work is needed to fully evaluate the effect of additives on reactivity of $Ca(OH)_2$ with NO.
- $CaSO_3$ and NaOH were found to promote the reactivity of $Ca(OH)_2$ and calcium silicates with NO. $CaSO_3$ did not significantly affect reactivity with SO_2.
- O_2 and SO_2 were necessary for NO removal. Reactivity with SO_2 was essentially unaffected by NO.

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Groundwater Treatment with Zero Air Emissions

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Air emissions from the treatment of volatile organic compound (VOC)–contaminated groundwater are a growing problem in the United States. Historically, air stripping has been used to remove VOCs from contaminated groundwater. Air stripping technology is a cross media treatment technique, i.e., it solves a groundwater problem by transferring contamination to the atmosphere.

In response to the air pollution problem created by air stripping, the public, air quality regulatory agencies, the federal government and private industry are exerting pressures to eliminate and/or reduce air emissions from the clean–up of contaminated groundwater. These forces make it desirable to consider alternative and innovative technologies for the treatment of groundwater contaminated with VOCs.

FACTORS TO BE CONSIDERED

Analysis of the groundwater remediation market has indicated that there are five key factors which motivate responsible parties to select treatment technologies with zero air emissions. The five factors are:

1) Specific regulatory limitations on the use of air strippers
2) Air toxics regulations
3) Community relations
4) Long–term public liability
5) SARA Section 121 requirements for the reduction of toxicity, mobility and volume of contaminants at National Priority List (NPL) sites

The major constraint on air emission controls is cost. This article will present data which demonstrate that oftentimes air emissions can be eliminated at a moderate cost.

Regulatory limitation of air strippers: The authors surveyed state and local air quality regulators throughout the nation which represented more than 50% of the population. All of the states surveyed had regulations addressing the issue of emissions from air strippers. Regulations fall into three different regulatory schemes: 1) Specific mass limitations; 2) Formalized risk assessment procedures; 3) Case–by–case analysis and risk assessment. Specific mass limitations vary from as little as one pound (0.454 kg) per day in the South Coast Air Quality Management District (SCAQMD) in southern California, to as much as 24 pounds (10.9 kg) a day in upper New York State [*1*, *2*]. Table 1 summarizes the data collected.

Air toxic regulations: A recent analysis of the status of air toxic regulations in the United States found that more than 46 of the 50 states either had or will soon have air

TABLE 1. REGIONAL AND STATE REGULATORY PROGRAMS AFFECTING THE DESIGN AND OPERATION OF AIR STRIPPERS

Specific Mass Limitations	Formalized Risk Assessment	Case by Case Analysis
New Jersey	Bay Area AQMD San Francisco, CA	Phoenix, AZ
New York	Florida	Pennsylvania
South Coast AQMD Los Angeles, CA	Illinois	Wyoming
Pima County, AZ	Ohio	Michigan
Puget Sound, WA		

TABLE 4. CASE STUDY 1
ANNUAL AIR STRIPPER/VAPOR PHASE CARBON ECONOMICS

	$/year
Capital Investment Annual Charge (20% of invested capital/year)	$ 10,000
Maintenance (5% of capital/year)	2,500
Electric Power for Air Stripper Blower and Dehumidifier (7 KW)	4,100
Carbon Consumption for Air Emission Control 100,000 kg @ $3.85/kg(a, b)	385,000
Air Monitoring	12,000
Total	$413,600
Total Cubic Meters Treated per Year:	43,170
Cost per Cubic Meter:	$9.58

(a) Beyers, W. D., "Control of Emissions from an Air Stripper Treating Contaminated Groundwater," *Environmental Progress*, p. 17, February 1988.

(b) Coutant, R. W., T. Zwick, and B. C. Kim, "Removal of Volatile Organics From Humidified Air Streams by Adsorption," report prepared for Air Force Engineering and Services Center, Battelle Columbus, Columbus, Ohio, 1987.

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Case Study 2—Effect of air toxic regulations on a northern California fleet refueling facility.

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Two alternative means of treatment were considered:

1) Air stripping with activated carbon vapor phase
2) UV peroxidation

Given the fact that the economics favor ultraviolet peroxidation and the process avoids the necessity of obtaining an air quality permit, the UV peroxidation system was selected. Table 6 contains water quality data. Tables 7 and 8 contain economic analysis of the two proposed systems.

TABLE 6. CASE STUDY 2
WATER QUALITY AND FLOW DATA

	Influent µg/l	Effluent µg/l
Toluene	7,000	100
Total Xylenes	3,500	100
Naphthalene	900	100
s-Butyl Benzene	900	100
1,3,5-Trimethyl Benzene	600	100
Ethyl Benzene	500	5
Benzene	5,000	0.7
1,2,4-Trimethyl Benzene	300	100
Bromoform	250	5
Chloroform	200	5
n-Butyl Benzene	175	100
n-Propyl Benzene	78	50
Methylene Chloride	20	5
1,2-Dichloroethane	10	5

Flow Rate: 125 gpm (0.47m^3/min)

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Electric Power (150 KW)	90,720
Total	$164,720
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TABLE 8. CASE STUDY 2
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	$/year
Capital Investment Annual Charge (20% of invested capital/year)	$ 20,000
Maintenance (5% of capital/year)	5,000
Electric Power for Air Stripper Blower and Dehumidifier (6 KW)	3,600
Carbon Consumption for Air Emission Control 40,910 kg @ $3.85/kg(a, b)	157,500
Air Monitoring(c)	12,000
Total	$198,100
Total Cubic Meters Treated per Year:	245,270
Cost per Cubic Meter:	$0.81

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TABLE 9. CASE STUDY 3
WATER QUALITY AND FLOW DATA

Contaminant	Influent μg/l	Effluent μg/l
Trichloroethylene	70	<1
Tetrachloroethylene	30	<1

Flow Rate: 100 gpm (0.378m^3/min)

Risk assessments were conducted as part of the permitting process and it was determined that no adverse consequences would occur due to the emissions. On this basis, the local air quality agency issued permits. However, a citizens' group from the local area objected to the concept and the facility decided it would be preferable to totally eliminate emissions.

Carbon adsorption on the offgas air stream was not seriously considered due to the very low inlet concentrations anticipated and the lack of reliable operating data at these low influent concentrations. A UV/peroxidation system was selected and was delivered to the site in October 1988 and was started up in January 1989. Table 9 contains water quality and flow data. The cost of the UV/peroxidation system was less than $50,000 a year.

The response from the community group was positive concerning the selection of a treatment process with zero air emissions. The group was quoted in the local paper as saying, "This is good news." The group went on further to state, "It is really positive to hear that they are listening to community concerns" [*10*].

Case Study 4—The effect of long term liability concerns on a New York State manufacturer.

A New York industrial firm was treating groundwater contaminated with trichloroethylene, vinyl chloride and numerous other industrial solvents. The treatment method being used was an air stripper—venting directly to the atmosphere. Management concern over the potential liability associated with vinyl chloride emissions and other chlorinated solvents led the company to investigate alternative means of treatment. The facility was operating in full compliance with all New York State and Federal air quality emission regulations.

Vapor phase carbon adsorption was not considered due to the fact that vinyl chloride in gaseous form is not adsorbable upon carbon. The company selected a UV/peroxidation system which was started up in July of 1988. Table 10 contains data on the industrial facility's water stream. The annual cost for the UV/peroxidation system was less than $50,000 a year.

TABLE 10. CASE STUDY 4
WATER QUALITY AND FLOW DATA

Contaminant	Influent μg/l	Effluent μg/l
Vinyl Chloride	500	<1
1,1-Dichloroethylene	50	<1
trans 1,2-Dichloroethylene	90	2
cis 1,2-Dichloroethylene	16,000	<40
Trichloroethylene	45,000	<50
Toluene	1,500	<2
Tetrarchloroethylene	100	<1
1,1,1-Trichloroethane	275	<150

Flow Rate: 15 gpm (0.057m^3/min)

Case Study 5—Effect of SARA Section 121 provisions on California industrial facility.

The SARA Section 121 provisions require the EPA to favor remediation programs which reduce the toxicity, mobility and volume of hazardous chemicals at Superfund sites. These provisions have been interpreted to disfavor separation treatment technologies, *i.e.*, air stripping and carbon adsorption, which separate contaminants from the water stream, as opposed to destruction technologies such as chemical oxidation [*11*].

These policies required a California industrial facility to evaluate two treatment schemes to remediate a groundwater contamination problem. Table 11 contains water quality and flow data. Economic data is summarized in Table 12 and 13.

The industrial facility selected UV/peroxidation and currently the project is out to bid. The project was completed during the summer of 1989.

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1,2-Dichloroethane	10	1
1,1,1-Trichloroethane	20	20
Methylene Chloride	5	5
Cis-1,2-Dichloroethylene	5	5
Chloroform	150	100

Flow Rate: 350 gpm (1.32m^3/min)

TABLE 12. CASE STUDY 5
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	$/year
Full Service Agreement Annual Fee (includes H_2O_2, Equipment, Maintenance, Emergency Service, Monthly Operating Report)	$122,800
Maintenance	Included in fee
Air Monitoring	NA
Electric Power (240 KW)	145,200
Total	$268,000
Total Cubic Meters Treated per Year:	686,600
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TABLE 13. CASE STUDY 5
LIQUID PHASE CARBON ADSORPTION ECONOMICS

	$/year
Capital Investment Annual Charge (20% of invested capital/year)	$ 30,000
Maintenance (5% of capital per year)	7,500
Air Monitoring	NA
Carbon Replacement (0.31 kg/m^3 based on laboratory isotherm data) 214,550 × $3.30/kg	708,000
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SUMMARY

Many variables must be evaluated in the development of groundwater remediation programs. Uncontrolled air emissions from air strippers can conflict with objectives of governmental agencies, the general public and private parties. In an effort to eliminate air emissions, many facilities are turning to the UV/peroxidation process, which not only has zero air emissions but can many times offer the lowest treatment cost. This technology should be considered, along with other existing and proven technologies in any groundwater remediation feasibility study.

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Sorbent and Ammonia Injection at Economizer Temperatures Upstream of a High–Temperature Baghouse

Paul Chu, Bill Downs, and Bob Holmes
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The current technology of choice—world–wide—for post–combustion NO_x control is selective catalytic reduction (SCR) with ammonia. The application of SCR to coal–fired units has proven to be somewhat more difficult than its application to natural gas and oil–fired units due to SO_2 poisoning of the catalyst, catalytic oxidation of SO_2 to SO_3, and erosion and fouling of the catalyst by fly ash [1]. These problems could be potentially diminished if SO_2 and particulate removal systems were placed upstream of the SCR reactor. However, this is not easily accomplished since SCR systems operate best in the temperature range of 600°F–800°F (315°C–425°C). Several SCR installations in Europe employ conventional flue gas desulfurization (FGD) and particulate control upstream of flue gas reheat and SCR. However, the flue gas reheat typically imposes a 1%–2% energy penalty [2]. Several recent technical developments now offer a technology whereby these limitations of SCR for coal applications can be alleviated. These technical developments are in the areas of high temperature filtration, improved SCR catalysts, and advances in sorbent injection. These advances have been incorporated into a patented process known as the SO_x–NO_x–Rox Box™ (SNRB) process. Briefly, this process consists of a "hot" baghouse employing woven ceramic fabric bags, a zeolite SCR catalyst incorporated into the baghouse, and the injection of either calcium–or sodium–based sorbent upstream of the baghouse (see Figure 1). This paper deals with the status and development of the SNRB process, including some results from recently completed pilot–plant tests performed under a contract with the Ohio Coal Development Office (OCDO).

THE SNRB PROCESS

A schematic representation of one possible arrangement of the SNRB process is depicted in Figure 2. In this version using a calcium–based sorbent, a mixture of hydrated lime and rehydrated baghouse recycle material are injected into the convective pass of a boiler upstream of the economizer, where the flue gas temperature may range from 800°F–1100°F (425°C–590°C). Simultaneous dehydration and sulfation of the sorbent begins immediately upon injection and continues as the flue gases pass through the boiler, economizer, and flues and into the hot baghouse. Using high temperature bags, the baghouse operates in the temperature range of 600°F–800°F (315°C–425°C). Anhydrous ammonia is injected upstream of the baghouse to reduce NO_x in the presence of a SCR catalyst. The SCR catalyst itself is incorporated into the baghouse, downstream of particulate collection. Thus, by the time the flue gas reaches the catalyst, the SO_2 concentrations have been reduced by 70%–90%, SO_3 concentrations have been reduced to below detectable levels, and particulates have been reduced to trace levels (99.9+% efficiency).

Since particulate and SO_x removal occur upstream of the air preheater, fouling and corrosion potential are substantially reduced, allowing the air preheater to operate at lower flue gas outlet temperatures. The additional energy recovery could improve boiler cycle efficiency by 1%–3%, compared to a system without SO_2 control. This would make the SNRB process one of few SO_x/NO_x removal processes that could increase—rather than decrease—a power plant's efficiency.

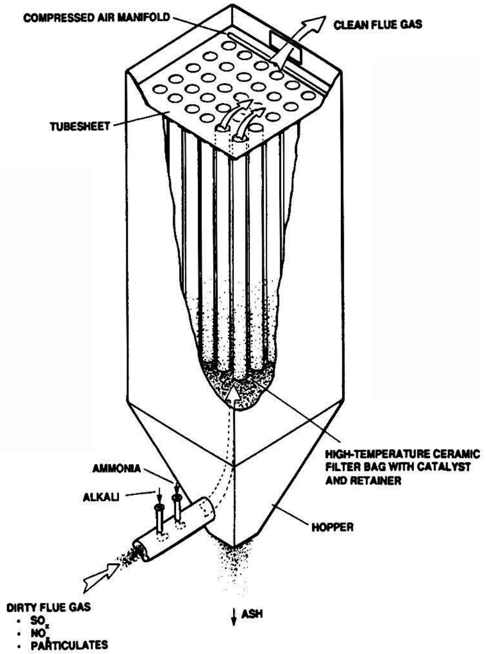

Figure 1. Schematic of the SO_x–NO_x–Rox Box™ (SNRB) process.

SNRB PROCESS DEVELOPMENT

Dry injection of various calcium– and sodium–based sorbents has been tested for retrofit applications mainly for SO_2 removal with NO_x removal as a secondary goal [*3–8*]. In 1982, the Babcock & Wilcox Company (B&W) evaluated low temperature (275°F [135°C]) nahcolite injection upstream of a pilot–scale baghouse. SO_2 removals from 70%–90% were typically achieved, with NO_x removals as high as 30%–40%.

Development of the SNRB process began in 1979 with a series of bench–scale investigations evaluating various fly ashes, transition metals, and a zeolite from the Norton Company as SCR catalysts. The initial concepts were to impregnate the catalyst onto the filter media or to coat the catalyst onto the filter media. NO_x reductions ranging from 40% to over 90% were achieved with the Norton zeolite catalyst.

The next phase of development of the SNRB process involved experiments using a small pilot–scale baghouse (350 acfm [600 m^3/hr]). These experiments involved the injection of ammonia and various "reagent/catalysts" upstream of the hot baghouse. To operate at temperatures up to 775°F (415°C), the baghouse utilized Nextel™ ceramic woven bags from 3M. These Nextel bags are able to operate at temperatures up to 2200°F (1200°C) [9]. Both calcium– and sodium–based reagent/catalysts were tested as well as the oxides of aluminum, copper, iron, and zinc. The concept was for the reagent/catalyst to react with SO_2 and NO_x while simultaneously catalyzing NO_x reduction by NH_3. No SCR catalysts were used in these experiments. At a normalized $NaHCO_3$:SO_x stoichiometry of 1.5, SO_2 and NO_x removals of 90% and 50%, respectively, were achieved.

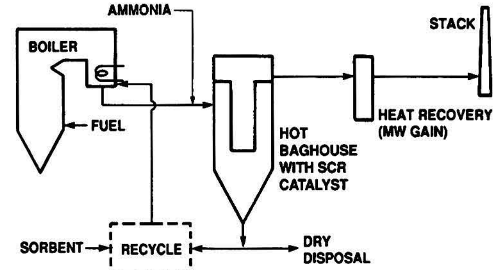

Figure 2. Schematic of one possible commercial SNRB process arrangement.

A sodium–based sorbent could have direct application in the western U.S. and especially the Green River basin area. However, due to reagent and disposal costs associated with sodium in the eastern U.S., a calcium–based reagent may be necessary. Further development of the SNRB process focused on two areas: 1) the ability to achieve NO_x removals up to 90%, and 2) identification of a calcium–based sorbent capable of 70%–90% SO_2 removal.

Based upon the above objectives, the project entered into its current phase of development, that is, an SCR catalyst was necessary to achieve consistent NO_x reductions of 90%. The zeolite catalyst, which B&W had tested earlier with some success, was developed by the Norton Company [*10*] and was chosen for use in the SNRB process. To facilitate integration of the catalyst into the SNRB process concept, a baghouse with a pulse jet cleaning system was utilized. In a pulse jet baghouse, particulate filtration occurs on the outside of the bag, thus permitting incorporation of the catalyst into the baghouse.

Because gas–solid reactions such as calcium/SO_2 are dependent upon the surface area of the reagent, it was anticipated that significant improvement could be achieved by substantially increasing the surface area of the reagent. Previous experimental work [*11, 12*] demonstrated that reactions between recycle lime and fly ash can create calcium silicate hydrates and calcium aluminum sulfate hydrates with surface areas from 100–300 m^2/g. These intermediates were shown to have enhanced reactivity toward SO_2. Based upon these results, B&W chose to explore this lime enhancement technology in this experimental program.

DESCRIPTION OF TEST FACILITY

A schematic of the test facility is depicted in Figure 3. The facility consisted of a pilot test furnace, an insulated

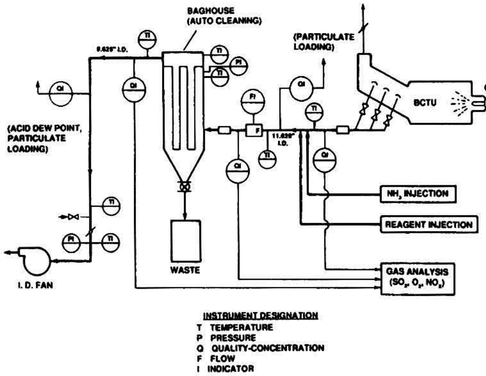

Figure 3. Schematic of 3000 acfm pilot test facility.

duct, a solids injection system, an ammonia injection system, a baghouse, and an induced draft (ID) fan. A blend of medium sulfur (2%–3%) bituminous coals was burned in the test furnace to produce flue gas. Depending upon the desired baghouse temperature, the coal feed rate was varied from 450–550 lb/hr (200–250 kg/hr) which is equivalent to 5.5–7.0 million Btu/hr (5.8–7.4 million kJ/hr). In addition, flue gases from three different locations in a water–cooled convection pass were blended together to help control the flue gas operating temperature. The flue gas composition was about 2200 ppm SO_2, 650 ppm NO_x, and 3% O_2. The sorbent injection system consisted of a solids feeder and an air eductor. Anhydrous ammonia from a cylinder was diluted with air before being injected into the flue gas.

The 3000 acfm (5000 m^3/hr) baghouse (see Figure 4) used for these experiments included an on–line pulse jet cleaning system, the zeolite catalyst incorporated into the baghouse, and the high temperature Nextel bags. Each bag measured 10 feet (3 meters) in length and 4.5 inches (11.4 cm) in diameter. Perforated retainers were used to support the ceramic bag. A vanadium–free variant of the commercial NC–300 series catalyst from the Norton Company was integrated into the baghouse to promote NO_x reduction by NH_3. For reasons of expediency, an alternative design was chosen to integrate the catalyst into the baghouse for these tests.

The duration of each test was typically 3 hours—one complete baghouse cleaning cycle. The concentrations of SO_2, NO_x, and O_2 were monitored at three locations—furnace outlet (prior to sorbent and ammonia injection), baghouse inlet, and baghouse outlet. The location of pressure and temperature measurements are shown in Figure 3.

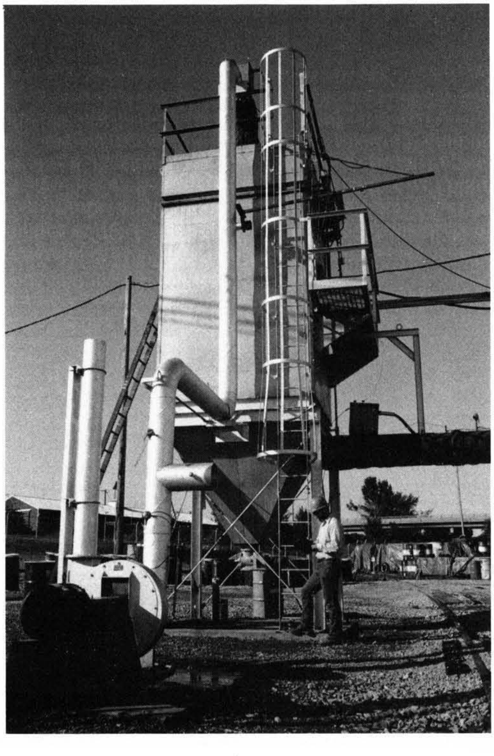

Figure 4. Pilot high–temperature baghouse.

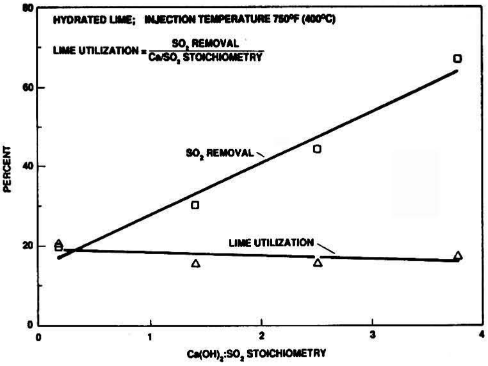

Figure 5. Effect of $Ca(OH)_2$:SO_2 stoichiometry.

RESULTS

Tests were conducted to evaluate several calcium–based sorbents in the SNRB process. The following calcium–based sorbents were examined:

- Hydrated lime
- Pressure–hydrated pebble lime
- Pebble lime (CaO) mixed with product recycle (fly ash, $CaSO_3$, $CaSO_4$, and unreacted $Ca(OH)_2$) and then pressure–hydrated

SO_2 Removal With Hydrated Lime

High calcium, commercial grade hydrated lime was used for the majority of the short term (2–3 hours) parametric tests and in the extended 30–hour run. The three variables that most influenced SO_2 removal were the Ca/SO_2 stoichiometry, injection temperature, and bag cleanliness/filter cake thickness.

The influence of the Ca/SO_2 stoichiometry is shown in Figure 5. These tests were conducted at an injection temperature of 750°F (400°C), which is well below the optimum temperature for SO_2 removal and lime utilization. However, Figure 5 illustrates that the SO_2 removal performance can be normalized by stoichiometry, over the range of stoichiometries tested (1 to 4). Sorbent utilization is equivalent to the SO_2 removal efficiency divided by the Ca/SO_2 stoichiometry.

The effect of temperature at the point of injection upon SO_2 removal was evaluated at 720°F–980°F (380°C–520°C) and is illustrated in Figure 6. SO_2 removal in-

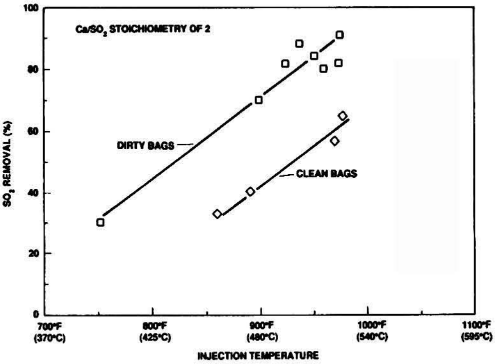

Figure 6. SO_2 removal with lime injection.

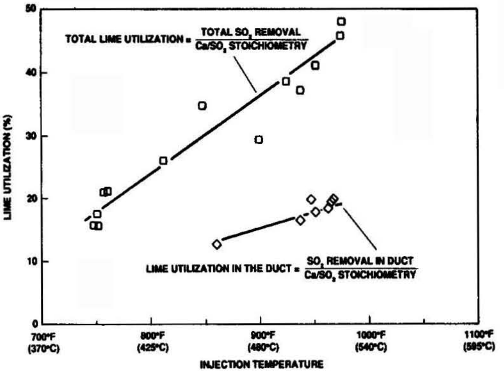

Figure 7. Effect of temperature.

creased significantly as the temperature rose. The effect of bag cleanliness is also illustrated in Figure 6. The overall lime utilization as well as the utilization in the duct upstream of the baghouse is illustrated in Figure 7. A significant portion of the SO_2 removal occurred in the duct upstream of the baghouse. Utilization in the duct was normalized by dividing the SO_2 removal in the duct by the stoichiometry. Similarly, baghouse SO_2 removal was normalized and illustrated in Figure 8 as a function of the baghouse inlet temperature.

The influence of bag cleanliness on lime utilization can be seen in two places. In Figure 9 as well as in Figure 6, data points taken shortly following baghouse cleaning cycles show reduced SO_2 removal and lime utilization. Likewise, Figure 10 depicts the SO_2 performance across the system during a 30–hour extended run. The times at which the bags were cleaned are identified on this plot. Note that SO_2 performance always diminished following bag cleaning, probably due to less filter cake on the bags. The baghouse cleaning technique consisted of cleaning one row of bags at a time, with the entire cycle lasting about 3 minutes.

The extent of $Ca(OH)_2$ dehydration of the hydrated lime was examined for several samples of baghouse solids during the parametric and extended tests. The results of the chemical analysis and thermogravimetric analysis (TGA) for three samples is presented in Table 1. A TGA of the hydrated lime is shown in Figure 11. The analysis of these samples reveal that over the temperature range tested (700°F–1000°F [370°C–540°C]), incomplete dehydration is likely.

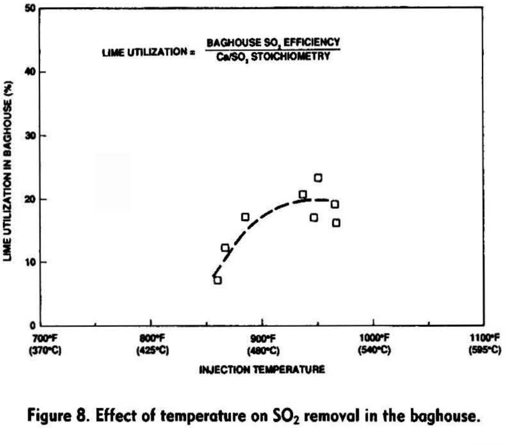

Figure 8. Effect of temperature on SO_2 removal in the baghouse.

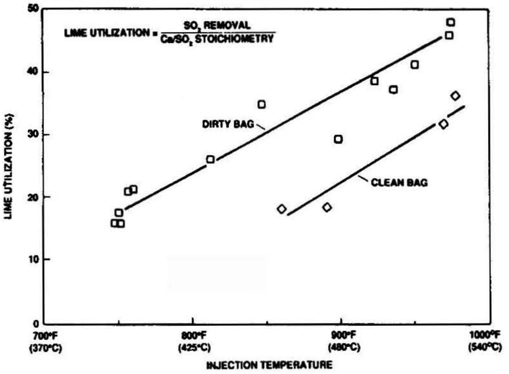

Figure 9. SO_2 removal across the filter cake.

Pressure–Hydrated Lime/Fly Ash Solids

A limited number of tests were conducted using various pressure–hydrated samples of lime and recycle solids mixtures. Pebble lime (CaO) was mixed with product recycle (consisting of fly ash, $CaSO_3$, $CaSO_4$, and unreacted $Ca(OH)_2$) and then pressure–hydrated in a batch pressure reactor. The product recycle solids consisted of baghouse solids from the hydrated lime tests. Various operating parameters were evaluated, including CaO:recycle ratio, $CaO{:}H_2O$ ratio, hydration temperatures, and hydration times. These tests were conducted at injection temperatures of 820°F–880°F (440°C–470°C). The results of these tests are shown in Figure 12. There does not appear to be any appreciable improvement over hydrated lime.

NO_x Removal

Experiments were conducted at catalyst temperatures from 500°F–850°F (260°C–455°C). This corresponded to injection temperatures from 575°F–1000°F (300°C–540°C). These SCR tests were conducted concurrent with the hydrated lime tests. The effect of catalyst bed temperature on NO_x removal is illustrated in Figure 13. Up to a catalyst temperature of 700°F (370°C), NO_x removal improved with increasing temperatures; above 700°F (370°C), NO_x removal leveled off. NO_x removals of up to 85% were achieved. Most of the tests were operated at an $NH_3{:}NO_x$ stoichiometry of about 0.9.

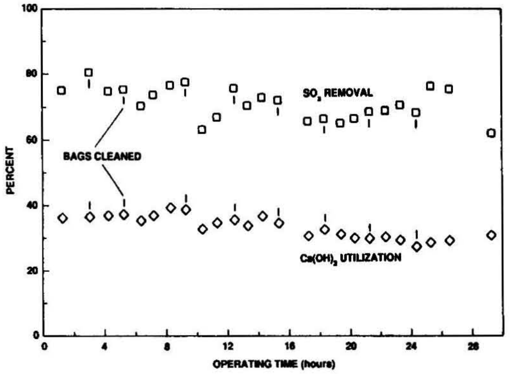

Figure 10. SO_2 removal and lime utilization during a 30–hour extended run.

TABLE 1. EXTENT OF $Ca(OH)_2$ DEHYDRATION

Injection Temperature	Dehydration	Lime Utilization
750°F (399°C)	41%	13%
950°F (510°C)	71%	32%
1000°F (540°C)	100%	42%

DISCUSSION

The rate of the SO_2–solid sorbent reaction has been observed by several investigators [*13, 14*] to be substantially enhanced if the solid sorbent is subjected to thermal decomposition while simultaneously reacting with SO_2. For example, in the LIMB (Limestone Injection/Multi–Stage Burner) system with lime/limestone injection into the upper furnace, the reaction of SO_2 with either $CaCO_3$ or $Ca(OH)_2$ is faster than the calcination reaction even though both the carbonate and hydroxide decompose almost instantaneously to CaO at 2300°F (1260°C). Likewise, in sodium–based systems, the use of sodium bicarbonate has repeatedly been shown to be superior to sodium carbonate in dry injection systems when the sodium bicarbonate decomposes rapidly to sodium carbonate. Explanation of this phenomenon has focused either upon the surface area enhancement that results when the sorbent decomposes, or upon chemical kinetics effects where the SO_2 reaction rate with the decomposition products is faster than with the primary sorbent.

Surface area enhancement effects have been tested by carefully precalcining sorbents to produce high surface areas and then exposing these decomposition products to SO_2. Invariably, these tests demonstrated lower utilizations than when simultaneous decomposition and SO_2 reaction occurs. One explanation for this effect is that the final surface area generated in the precalcined sorbent may be substantially less than the maximum surface area generated during calcining. That is, some sintering of the decomposition product may occur during calcining.

The intrinsic reaction rate of SO_2 with $Ca(OH)_2$ or CaO at the temperature range of these tests (700°F–1000°F [370°C–540°C]) is not known with certainty. However, even if the intrinsic reactivity of these two sorbents were substantially different, most investigators have deduced that the rate limiting step is diffusion through the product layer on the surface of the sorbent (calcined or uncalcined).

An alternative explanation for the apparent synergism between SO_2 reaction and thermal decomposition is offered as follows. Upon injection of calcium hydroxide into the flue gas, both SO_2 reaction and dehydration commence immediately.

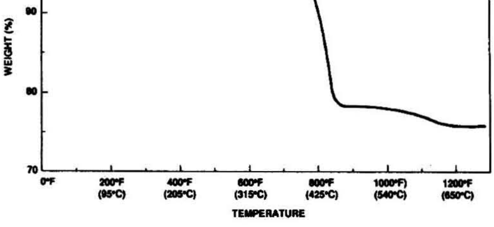

Figure 11. Thermogravimetric analysis (TGA) of reagent–grade $Ca(OH)_2$.

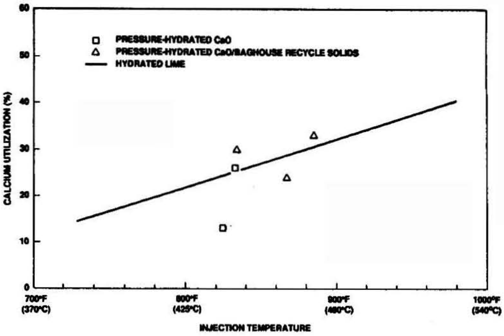

Figure 12. Pressure–hydrated lime/fly ash sorbents.

$$Ca(OH)_{2(s)} + SO_{2(g)} \rightarrow CaSO_{3(s)} + H_2O_{(g)} \tag{1}$$

$$Ca(OH)_{2(s)} + \text{heat} \rightarrow CaO_{(s)} + H_2O_{(g)} \tag{2}$$

The decomposition product, CaO, may react further with SO_2.

$$CaO_{(s)} + SO_{2(g)} \rightarrow CaSO_{3(s)} \tag{3}$$

In addition, the $CaSO_3$ reaction product may oxidize to $CaSO_4$.

$$CaSO_{3(s)} + 1/2\ O_{2(g)} \rightarrow CaSO_{4(s)} \tag{4}$$

In the operating temperature zone of 700°F–1000°F (370°C–540°C), $Ca(OH)_2$ dehydration is relatively slow (compared to the Ca/SO_2 reaction) and can continue for several seconds. By contrast, dehydration of $Ca(OH)_2$ in the LIMB system where sorbent is injected at about 2300°F (1260°C) takes no more than about 0.1 second. This synergistic effect of simultaneous dehydration along with reaction with SO_2 can continue from the point of injection and into the baghouse. The available surface of $Ca(OH)_2$ would soon be consumed and converted to $CaSO_3/CaSO_4$. Subsequent reaction of SO_2 would be slowed by its diffusion through the product layer. However, since the dehydration reaction is dependent only on the sorbent temperature and water partial pressure, the dehydration reaction proceeds in spite of the sulfite/sulfate surface. The net effect is that internal pore passages are created by the escaping water vapor, thus providing pore passages for SO_2 diffusion into the interior of the sorbent particle.

The rate of $Ca(OH)_2$ dehydration is dependent upon the temperature and water partial pressure of the flue gas. A thermogravimetric analysis of the $Ca(OH)_2$ sorbent is shown in Figure 11. From 765°F–850°F (405°C–455°C),

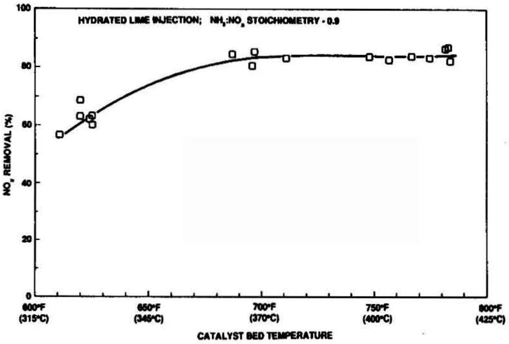

Figure 13. Effect of temperature on NO_x removal.

about 85% of the waters of hydration are driven off, with the remaining 15% coming off between 1020°F–1210°F (550°C–655°C). The solids analyses revealed that $Ca(OH)_2$ dehydration and lime utilization both increased at the higher injection temperatures (Table 1). However, the rate of dehydration may also affect sorbent utilization. A temperature window for hydrated lime injection may exist where the simultaneous dehydration of $Ca(OH)_2$ and reaction of CaO/SO_2 is optimized.

An advantage of a baghouse is that the Ca/SO_2 reactions can take place in the additional residence time of the baghouse and as the flue gas passes through the filter cake solids. At a stoichiometry of 2, SO_2 removals up to 40% were measured across the baghouse. Lime utilization in the baghouse appeared to be optimized at a baghouse inlet temperature of 900°F (480°C), which corresponded to an injection temperature of 1000°F (540°C). After cleaning the bags, a drop in SO_2 removal of 5–15 percentage points was immediately observed. With continued lime injection, SO_2 removal proceeded to increase with longer operating time, *i.e.*, increasing filter cake thickness. The University of North Dakota evaluated lime injection at 1500°F (815°C), upstream of a baghouse operating at 940°F (505°C). Overall lime utilizations of 40% were measured, with less than 5% SO_2 removal across the baghouse [*3*].

One potential benefit of the SNRB process is its ability to improve heat recovery and boiler efficiency. Since the particulate and sulfur removal occur upstream of the air heater, the fouling and corrosion potential, *i.e.*, acid dew point, are reduced downstream of the SNRB process. This depressed acid dew point allows operation of the air heater, located downstream of the baghouse, at a lower flue gas exit temperature, thereby increasing heat recovery. The acid dew point at the baghouse outlet was measured in this work to be less than 170°F (77°C)—the lower detection limit of the acid dew point meter used for the measurements.

NO_x REMOVAL

In the presence of the Norton zeolite catalyst, NH_3 will selectively reduce NO_x to nitrogen and water.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (5)$$

The Norton catalyst is effective in the temperature range of 480°F–970°F (250°C–520°C).

The pilot-scale NO_x removal performance was less than expected based upon previous Norton operating experience and data. Above 700°F (370°C), NO_x removal leveled off (see Figure 13). At the operating conditions, NO_x removals up to 90% were expected. A possible reason for the reduced NO_x performance is that some flue gas bypassing around the catalyst may have occurred. For reasons of expediency, an alternative catalyst design was used to incorporate the catalyst into the baghouse. In a commercial system, integration of the catalyst would be designed so as to prevent any sneakage from occurring.

ECONOMIC EVALUATION

A preliminary economic analysis of the SNRB process using calcium-based sorbents was made. This analysis was applied to the 500–MW_e plant described in a 1988 DOE Program Opportunity Notice for Clean Coal 2 [*15*]. Assuming 90% SO_2 and NO_x removal in the 500–MW_e plant, the cost of removal was estimated to be $512 per ton of SO_2 and NO_x removed. For a comparable system employing SCR and wet FGD, the cost would be $700–$760 per ton of SO_2 and NO_x removed.

One potential benefit of the SNRB process is its ability to improve heat recovery and boiler efficiency. As stated previously, since the particulate and sulfur removal occur upstream of the air heater, the fouling and corrosion potential are reduced. Estimates for a typical power plant burning high sulfur coal suggest that flue gas at the air heater outlet could be safely lowered to 175°F–200°F (80°C–95°C) when using the SNRB process. When compared to conventional practice with coal-fired boilers, where the exit gas temperature is maintained above 250°F–320°F (120°C–160°C), this represents an incremental energy recovery of about 1%–3%.

CONCLUSIONS

Hydrated lime injection at economizer temperatures is feasible. Overall SO_2 removal improved with increasing lime injection temperatures up to 1000°F (540°C). An optimum temperature window may exist for SO_2 removal and $Ca(OH)_2$ dehydration. At injection temperatures above 900°F (440°C), SO_2 removals from 70%–85% were achieved at a $Ca(OH)_2$:SO_2 stoichiometry of 2. Of that overall removal, SO_2 removals of 40% were accomplished in the baghouse. Substantial SO_2 removal was obtained across the filter cake. After the bags were cleaned, a decrease in SO_2 removal of 5–15 percentage points was observed.

At an injection temperature of 850°F (455°C), the pressure-hydrated CaO/baghouse recycle material was not significantly more reactive than commercially hydrated lime (hydration at 1 atmosphere).

NO_x removals greater than 80% were achieved at a catalyst temperature ranging from 700°F–800°F (370°C–425°C) and at an NH_3:NO_x stoichiometry of 0.9.

The acid dew point of the flue gas at the baghouse outlet was less than 170°F (77°C), which was the lower detection limit of the acid dew point meter. Thus, the SNRB process potentially can operate at air heater outlet temperatures much lower than conventional systems without SO_2 control.

ACKNOWLEDGMENTS

The authors thank Dave Berger and Howard Johnson of the Ohio Coal Development Office (OCDO) for supporting this pilot-scale research program. In addition, we would like to thank 3M for supplying the Nextel bags, the Norton Company for providing the zeolite SCR catalyst, and both for their technical support and assistance.

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Minimization of Chromium-Contaminated Wastewater at a Plating Facility in the Eastern United States

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The Oak Ridge National Laboratory (ORNL) is conducting a hazardous waste minimization program at an industrial plating facility located in the Eastern United States. A detailed investigation of the existing facility was conducted by ORNL which indicated that chromium was the major source of contamination. Several improvements in the operation of the facility were implemented which reduced the quantity of chromium lost from the facility by ~85%. The remaining chromium-contaminated wastewater streams will be treated by reverse osmosis (RO) followed by evaporation of the RO concentrate for further volume reduction. This paper discusses (1) the plating shop modifications which resulted in an 85% reduction of the quantity of chromium contamination exiting the plating facility, (2) the results of RO pilot-scale tests, and (3) start up of the full-scale RO/evaporator system the plating facility.

INTRODUCTION

The local metropolitan sewer district (MSD) established permit limits (see Table 1) for the plant discharge which reflected the Environmental Protection Agency's pretreatment limits for metal finishing waste. The permit required that a sample of the waste stream from the plating shop be taken and analyzed monthly. These data are then reported to the MSD. The results of the monthly analyses indicated that the chromium concentration approached, but did not violate, its maximum daily allowable discharge limit on several occasions (Walker, *et al.*, 1987) [*1*]. Because a limited number of analyses had been run on the effluent stream from the plating shop (12

TABLE 1. DISCHARGE LIMITS FOR THE PLATING SHOP EFFLUENT STREAM (MG/L)

Parameter	Maximum for any one day	Average of daily values for 30 consecutive days
Cadmium	0.69	0.26
Chromium	2.77	1.71
Copper	3.38	2.07
Lead	0.69	0.43
Nickel	3.98	2.38
Silver	0.43	0.24
Zinc	2.61	1.48
Cyanide	1.20	0.65

TABLE 2. SUMMARY OF ANALYTICAL RESULTS FOR METALS AND CYANIDE

	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Pb (mg/L)	Ni (mg/L)	Ag (mg/L)	Zn (mg/L)	Cn (mg/L)
High	0.24	6.80	0.51	0.30	0.15	0.03	0.95	0.54
Low	0.03	0.32	0.01	<0.10	<0.05	<0.01	0.12	<0.01
Average	0.07	1.33	0.10	<0.11	<0.07	<0.01	0.32	<0.03

samples over a one year period), a characterization study was conducted on the effluent stream from the plating shop over 30 consecutive days of operation. The results of this characterization study are summarized in Table 2. As can be seen, the concentration of cyanide and all metals, except chromium, were present at concentrations well below the discharge limits. The concentration of chromium in the plating shop effluent for the 30–consecutive–operating–day period, along with the allowable MSD maximum daily allowable concentration, is presented graphically in Figure 1. It can be seen that during this period chromium was in violation of the daily discharge limit for 4 days. The 30–d–average chromium concentration during this period was 1.33 mg/L. During the sampling period, the inventory of parts to be plated was below normal; thus, the effluent contaminant concentrations were lower than normally would have been expected. During periods of high plating activity, the 30–d–average chromium concentration could approach the 30–d limit of 1.71 mg/L. The results of this characterization study indicated that chromium contamination was the major problem area for the plating shop.

The major sources of chromium contamination for the plating shop were identified. These sources, along with the estimated quantity produced by each, are presented in Table 3. Several improvements in the operation of the plating shop were made to reduce the quantity of chromium–contaminated wastewater generated. These improvements included: (1) installation of a closed–loop rinsing system with zero discharge on the chrome plating line, (2) utilization of a "new bright–dip formula" which contained ~75% less chromium that the previous formula, and (3) replacement of the dichromate deoxidizer on the chromate conversion line with a chromium–free deoxidizer (Walker, *et al.*, 1987) [*1*]. A new ventilation system was also being installed to eliminate the chromium which collects in the defunct ventilation scrubbers. These improvements in the operation reduced the quantity of chromium contamination by as much as 85%.

With the improvements noted above, the remaining major sources of chromium contamination were the rinse water from the gun barrel line (~80 kg chromium/year) and the rinse water from the bright-dip line (~65 kg/year). The gun line consists of a chrome–plating bath, an electropolish bath, and a rinse tank. The bright–dip line contains a caustic paint stripping bath, a muriatic acid bath, a bright–dip bath (sulfuric acid + sodium dichromate), and a rinse tank. A system consisting of RO coupled with concentrate evaporation was recommended to meet the sponsors' objective for the demonstration of innovative wastewater treatment technology which will produce information useful for treating similar wastewaters at other facilities. Evaporation of the RO concentrate will maximize waste volume reduction and process flexibility. A schematic diagram of the treatment system recommended for use is presented in Figure 2.

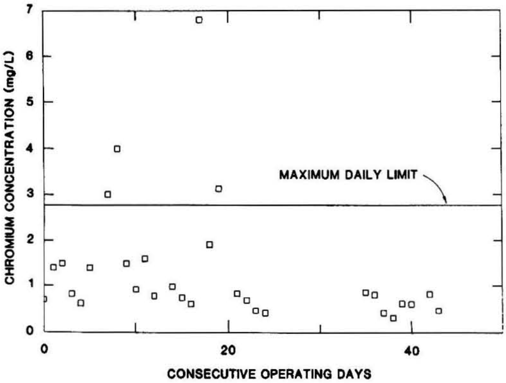

Figure 1. Concentration of chromium in the plating shop effluent for 30 consecutive operating days.

PILOT–SCALE STUDIES

Pilot studies were conducted at the plant site to determine if the rinse water could be successfully treated by RO. Polyamide spiral wound membranes were used in these studies. A block diagram of the RO system is presented in Figure 3 to facilitate definition of key process parameters. In Figure 3, F, P, C, CR = flow rate of the feed, permeate, concentrate, and recycle, respectively; and x, y, z = contaminant concentration in the feed, concentrate, and permeate, respectively. Recovery (R) represents the fraction (as a percentage) of the feed that reports to the permeate and is calculated as indicated in the following equation:

$$R = \frac{P}{F} \times 100$$

Rejection is a measure of separation (*i.e.*, how well the membrane removes the contaminants of interest present in the feed stream). Rejection can be calculated on a system basis or for the membrane, but the system and membrane rejections can be related via material balance relationships. The material balance envelope for each case is indicated in Figures 3a and 3b. System rejection (γ_s) is calculated via

$$\gamma_s = \left[1 - \left(\frac{z}{x}\right)\right](100)$$

and Membrane rejection (γ_m) is calculated via the equation

TABLE 3. ESTIMATED QUANTITY OF CHROMIUM LOST FROM MAJOR SOURCES

Source	Estimated quantity during 1986 (kg)
Chrome plating line	155
Gun barrel line	80
Ventilation scrubbers*	240
Chromate conversion line	525
Bright–dip line	260

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* This quantity of chromium was recovered from the ventilation scrubbers and recycled to the plating baths. The amount of chromium lost to the sewer was not determined.

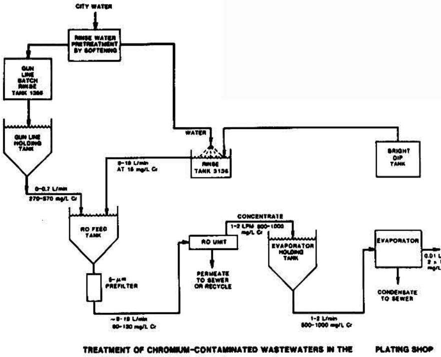

Figure 2. Process flow diagram.

$$\gamma_m = \left[1 - \left(\frac{z}{\bar{x}}\right)\right](100)$$

where

$\bar{x}$ = average concentration of contaminant to which the membrane is exposed.

To enable prediction of process performance at various system operating conditions, it is necessary to know the membrane rejection of the contaminants of interest and how the membrane rejection varies with contaminant concentration.

Data gathered from the treatment of the rinse water generated following the plating of a [13-cm (5-in.-diam)] gun barrel are presented in Figures 4, 5, and 6. This gun barrel rinse water had a chromium concentration varying from 55 to 85 mg/L and a pH of ~3.0. As can be seen in Figure 4, the system recovery was increased from 85% to 95% during this 300 h of operation. Figure 5 presents the chromium rejection for the system and for the membrane (see Figure 3 for definition of system and membrane rejections) during this same period. The system chromium rejection was ~95%, while the membrane chromium rejection was >99%. The permeate flow with time during this period is presented in Figure 6. As expected, the permeate flow fell rapidly during the first several hours of operation. This decline in permeate flux is typical with new membranes and was due to initial solids deposition. After ~30 h of operation, the decline in permeate flux slowed and the flow leveled out at 550 to 650 mL/min. The brief, sharp increases in the permeate flow followed system shutdowns. Prior to shutting down the system, the membrane was flushed with clean water at a high velocity. This flushing washed solids from the membrane surface and resulted in a higher permeate flux when the system was restarted. However, the increased flux was short lived, and the preshutdown permeate flux level was reached after a few hours of operation. The data from RO treatment of the gun line rinse waters indicated that RO treatment of this waste stream was feasible using a 1–5 μm filter for pretreatment.

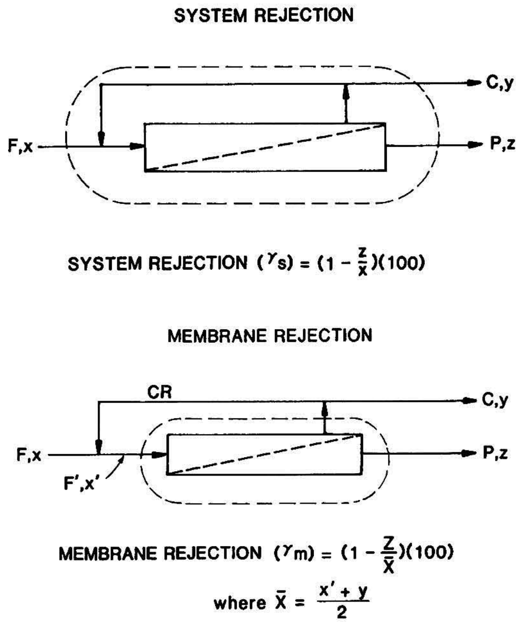

Figure 3. Material balance envelope for calculation of the system (3a) and membrane (3b) rejections.

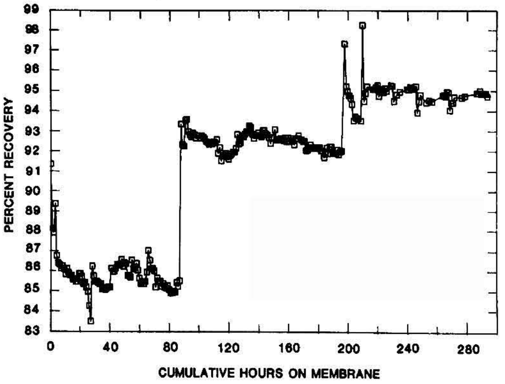

Figure 4. System recovery with time while treating the gun line rinse waters.

Data from operation of the RO pilot unit on the rinse water from the "bright–dipping" operations are presented in Figures 7 and 8. During this test, the system recovery was ~95% and, as seen in Figure 7, both the system and membrane chromium rejection exceeded 98%. The permeate flow with time during operation on the "bright–dip" rinse water is presented in Figure 8. The permeate flux seemed to level out with a permeate flow rate of 500 to 600 mL/min after ~40 h of operation. This was similar to the result obtained with the rinse waters from the gun line. However, at ~180 h of operation the

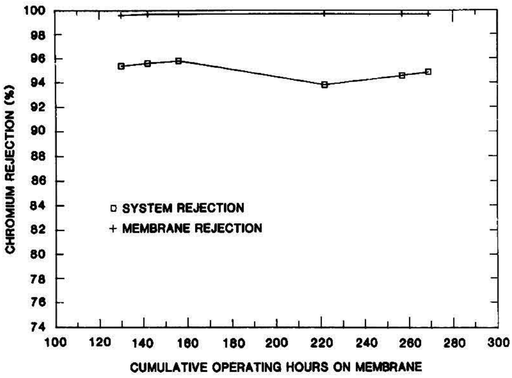

Figure 5. Chromium rejection with time while testing the gun line rinse.

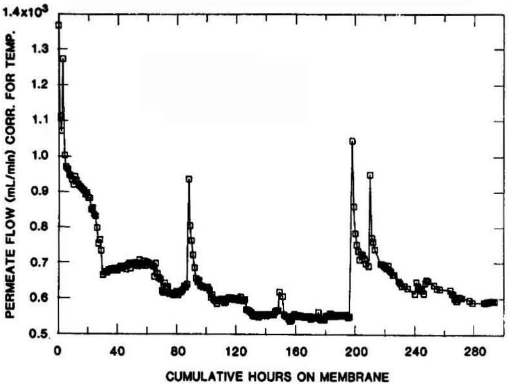

Figure 6. Permeate flow with time while treating the gun line rinse waters.

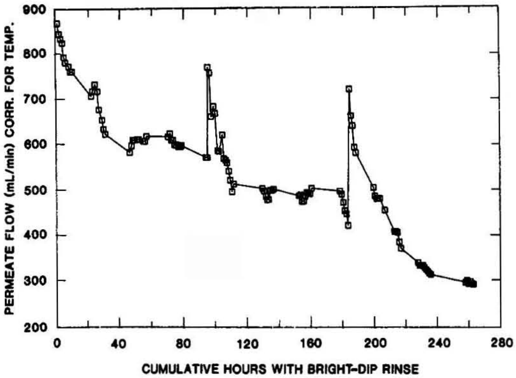

Figure 8. Permeate flow with time while treating the bright–dip rinse waters.

permeate flux again began to decline rapidly. This decline coincided with the introduction of a new batch of "bright–dip" rinse water. The quality of bright–dip rinse water varies considerably from batch to batch. For instance, the pH of the batch of rinse water used to feed the RO unit from 0 to 180 h, in Figure 8, was ~3.0. The new batch, introduced at 180 h, had a pH of ~7.0. The quality of the rinse water is dependent on the quantity and types of parts being plated.

Several runs were made with the bright–dip rinse waters to determine the best pretreatment for this waste stream. In these runs, the pH of the RO feed was varied from ~2.5 to 8 and the RO recovery was also varied. In all cases, the feed was passed through a 1 μm filter prior to entering the RO membrane. The decrease in the permeate flux was independent of pH and RO recovery, and varied from one batch of bright–dip rinse to the next. None of the pretreatment options tested, which included different filtering systems, pH adjustment, and dispersants, were effective in reducing the decline in the permeate flux.

Since pretreatment proved ineffective for the bright–dip rinse stream, the possibility of cleaning the membrane to restore the lost permeate flux was examined. Phosphoric acid cleaners, generally used for mineral fouling, proved ineffective. Alkaline cleaners (a mixture of sodium hydroxide and sodium lauryl sulfate), used for organic fouling, also proved ineffective. The most effective method found for cleaning the membranes used on the bright–dip rinse waters was a 1% solution of ethylenediaminetetraaceticacid (EDTA) at a pH of ~11.5. By cleaning with a 1% solution of EDTA, the permeate flux was restored to 93% of its initial value. Therefore, in designing the full–scale treatment system, the RO unit was oversized so that the unit could operate for several weeks before the permeate flux had declined enough to require cleaning of the membrane. This method should be particularly effective at the present facility because the bright–dipping operation occurs only one day a week, and the treatment system was designed with holding tanks sized to contain the entire waste stream from the bright–dipping operation. Therefore, the bright–dip rinse stream can be treated over a period of several days and the RO unit can then be shut down and cleaned, without the waste stream going to the sewer. The evaporator, which was included in the system design for further volume reduction of the RO concentrate, also allows some flexibility in the treatment system operation. With the holding capacity designed into the treatment system, the evaporator can treat the entire waste load from the bright–dipping operation during a one week period, if problems should occur with the RO unit.

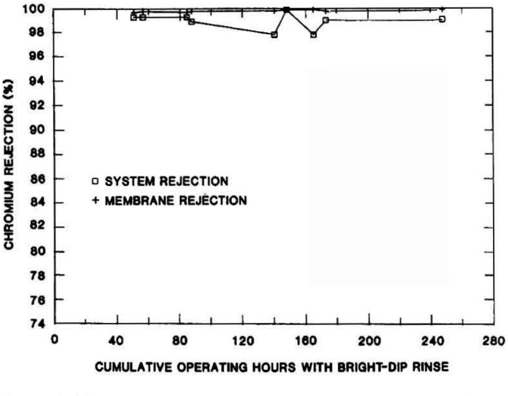

Figure 7. Chromium rejection with time while treating the bright–dip rinse waters.

START UP OF THE FULL-SCALE SYSTEM

After completion of the pilot tests, a full–scale unit was constructed and transported to the industrial plating shop. The treatment system was built inside a mobile trailer so that the project sponsor could use the system to test or treat wastewaters at other plating facilities, if necessary. Wastewater which had been stored on site was used to test the treatment system during startup. During this short–term test, the RO rejection of chromium exceeded 98%, which was typical of the results obtained during the pilot studies. The permeate flux decreased with time; however, the decline in the permeate rate with time was less than the decline found in the pilot studies when the pilot unit was started up on a new membrane. The RO unit was not run long enough to evaluate the loss in permeate flux with time. Cleaning the membranes with a mixture of phosphoric acid returned the permeate flux to its initial value.

SUMMARY

A characterization study of the effluent from the plating shop indicated that the effluent contained chromium concentrations which were, at times, in violation of the permit discharge limits. Several improvements in the operation of the plating shop were implemented which reduced the quantity of chromium in the effluent by as much as 85%. The use of RO and evaporation were recommended to meet the sponsors objective for the demonstration of innovative wastewater treatment technology. This technique would be applied to the two remaining major sources of chromium contamination (the gun line rinse and the bright–dip rinse). Pilot–scale RO tests indicated that the gun line rinse waters could be successfully treated by RO using a 1 to 5 mμ prefilter. Pretreatment of the bright–dip rinse water proved to be ineffective; however, cleaning the membrane with a 1% solution of EDTA restored the permeate flux to 93% of its initial value. This allowed the use of RO treatment of the bright–dip rinse by oversizing the RO unit to take into account the expected loss in permeate flux. The full–scale treatment unit was built, transported to the industrial facility, and started up using wastewater stored at the facility. The rejection of chromium exceeded 98%, which was typical of the chromium rejections in the pilot studies. During this short–term test, the permeate flux decreased with time. The decrease in permeate flux with time was less than the decrease obtained during the pilot operation when the pilot unit was started up on a new membrane. The RO system was not run long enough to completely evaluate the loss in permeate flux with time. The lost permeate flux was restored by cleaning with a mixture of phosphoric acid.

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Biodegradation of Chlorinated Hydrocarbons in an Immobilized Bed Reactor

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A 75 liter immobilized microbe biological reactor with a bed retention time of 20.5 hours was used in a continuous flow mode to remediate contaminated groundwater containing ethylene dichloride (EDC), tetrachloroethylene, and trichloroethylene, with EDC being the predominant contaminant. The reactor was initially seeded with Xanthobacter autotrophicus, *a demonstrated halogenated aliphatic substrate utilizer. The reactor was operated for forty-two days. Material balance determinations for primary volatile aliphatics of concern indicated an average of 90.2% mineralization of EDC, 81.7% of the trichlorethylene (TCE) and 64.0% of the tetrachlorethylene (TeCE). In addition to* Xanthobacter autotrophicus, *four indigenous bacterial species from the groundwater had successfully acclimated to the reactor bed.*

INTRODUCTION

Biological treatment using an immobilized microbial consortia has been studied by several researchers. Portier *et al.* [*1*] used an immobilized substrate to enhance PCB degradation, Chibata [2] studied immobilization to enhance aspartase deactivation, and Welsh *et al.* [3] tested eight different immobilization supports for effectiveness in biological treatment. There has also been an interest in the ability of bacteria to degrade halogenated hydrocarbons (Vogel *et al.* [*4*], Livesey and Anders [5], Friday and Portier [6]), and the species ethylene dichloride in particular. (Stucki *et al.* [*7*], Bouwer and McCarty [8], Belay and Daniels [9], and Janssen *et al.* [*10*].) The use of biological reactors is a low maintenance, cost effective method of removing hazardous components from groundwater or wastewater streams. An advantage of biological treatment over physical separation techniques is that the hazardous material is chemically altered to nontoxic material or mineralized to CO_2 and biomass. With physical separation the hazardous material is recovered, but still requires disposal.

In this study, a biological reactor was used to remediate groundwater contaminated with chlorinated hydrocarbons. The major contaminants were ethylene dichloride (EDC), 1,2-$C_2H_4Cl_2$, trichloroethylene (TCE), C_2HCl_3, and tetrachlorethylene (TeCE), C_2Cl_4. The rationale of these continuous flow tests was to identify operating parameters and related materials handling needs to successfully design and operate such a system as a permanent remediation facility. Additionally, the evaluation of mineralization rates for minor halogenated aliphatic contaminants in the ground water was of interest both from a microbial physiological perspective as well as a need to include these data in reactor design and process scale-up considerations.

REACTOR DESIGN

A schematic of the 75 liter reactor used to remediate site groundwater is shown in Figure 1. Contaminated groundwater with minimal nutrient addition for biomass growth optimization was fed into the reactor at 1.5 L/h. The feed entered the recycle line on the suction side of the recycle pump. The recycle stream was then aerated using 300 standard cc/min of air at 27 psi in a co-mingling jet configuration. The air and liquid stream are in contact through the aerator, where oxygen dissolves into the liquid stream. The liquid leaves the aerator with a dissolved oxygen (DO) level of 2.5 mg/L. The feed stream then entered a heated reactor maintained at 30°C. Some of the liquid was discharged out the reactor discharge line to maintain a constant liquid level in the reactor. The remaining aerated liquid stream enters into the packed bed section of the reactor and flows down through the bed.

The bed was packed with spherical diatomaceous earth beads (Manville R630 carrier). After leaving the bed the treated stream enters the recycle line; the recycle flow rate was 1.5 gallons per minute (gpm). Having a high recycle flow rate to feed flow rate ratio provided for good mixing in the reactor and allowed the reactor feed to maintain a high DO content. In this manner, the immobilized microbe bioreactor operated as a continuously stirred tank reactor (CSTR), wherein chlorinated aliphatic levels in the reactor approached levels in the reactor discharge line.

EXPERIMENTAL APPROACH

In order to develop a healthy biomass with which to treat the groundwater, the reactor was inoculated with 3 liters of a fermented broth containing *Xanthobacter autotrophicus* and 1.5 liters of nutrient solution. The reactor was then operated in a batch mode to develop the bacterial biomass density and to allow for complete colonization and subsequent immobilization on the carrier bed.

After the biomass had become established in the bed, the reactor was fed the contaminated groundwater for 42 days at a feed rate of 1.5 liters/min. This initial 42-day period allowed the reactor bed to be acclimated to chlorinated aliphatics in the groundwater and also allowed the indigenous bacterial species in the groundwater to develop a secondary biomass niche in the packed bed. The intent of the original experiment was to have only *Xanthobacter autotrophicus* as the active bioremediation species in the bed. However, due to the nature of the bacteria in the groundwater, it was impossible to keep all indigenous microflora out of the reactor bed with its ideal growing conditions. The resulting layered bacterial mix was used in the bed for the reactor experiments.

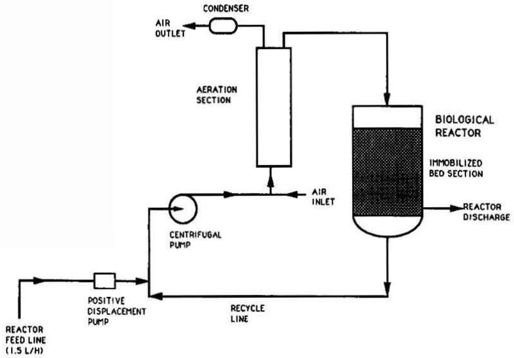

Figure 1. Schematic diagram of the reactor unit.

The reactor was operated for a second 42-day period during which material balance data were collected. Composition was determined by gas chromatography (FID detector; Carbopak B packed capillary column). Three chemical species were targeted to determine how effective the reactor would be in removing them from the feed stream. These were ethylene dichloride (EDC), 1,2-$C_2H_4Cl_2$; trichloroethylene (TCE), C_2HCl_3; and tetrachlorethylene (TeCE), C_2Cl_4. The feed rate was 1.5 liters/h of groundwater and the average contaminant loading was 226 mg/L for EDC, 10.9 mg/L for TCE, and 2.5 mg/L for TeCE.

RESULTS

Operating conditions for the 42-day test period are shown in Figure 2. Figure 2(a) presents the dissolved oxygen in the reactor, 2(b) shows the reactor pH, and 2(c) gives the temperature. The pH and temperature were held constant throughout the test, with pH ranging from 6.5 to 7.5 and the temperature from 86°C to 102°C. The dissolved oxygen content in the reactor varied over a wide range, from 1.2 mg/L to 3.3 mg/L.

Reactor efficiency in degrading EDC is shown in Figure 3. The average EDC reduction was 90.8% of the EDC in the feed stream. A calculation of the air stripping rate

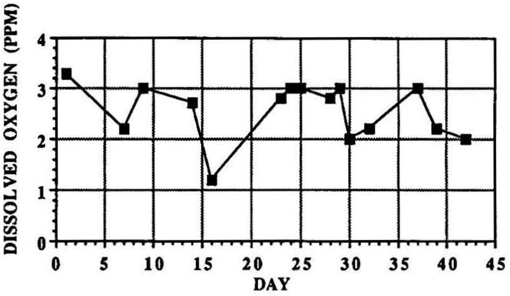

Figure 2a. Dissolved oxygen levels in the reactor.

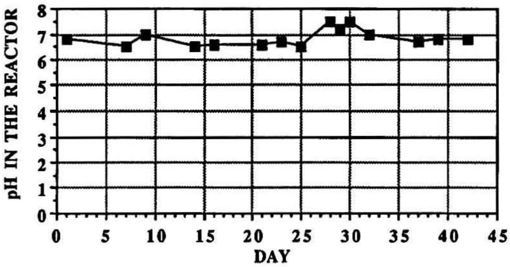

Figure 2b. pH in the reactor.

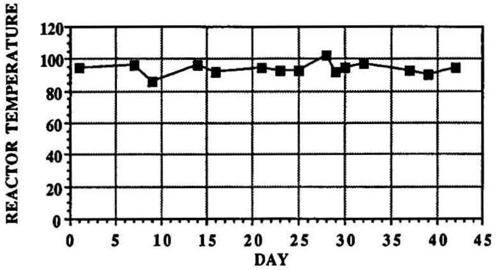

Figure 2c. Temperature of the reactor.

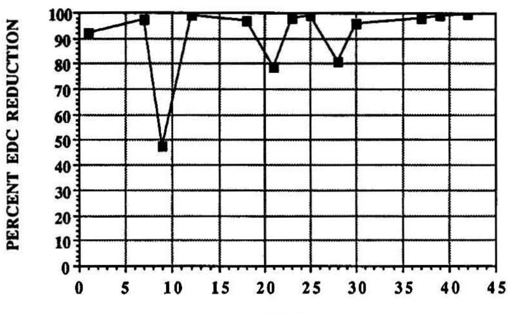

Figure 3. Percent removal of ethylene dichloride (EDC) from the reactor feed stream.

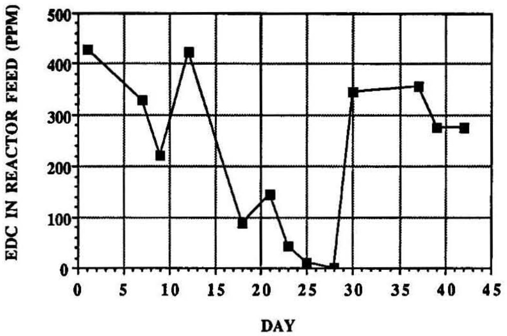

Figure 4. Ethylene dichloride concentration in the reactor feed stream.

in the reactor showed that only 0.4% of the EDC was removed in the air stream by stripping. The Henry's law constants used in the stripping calculations are given in Table 1. The EDC feed rate fluctuated dramatically, as seen in Figure 4. The concentration of EDC in the feed stream ranged from 0.8 mg/L to 428 mg/L, with an average of 226 mg/L. The removal efficiency was above 75% for all measurements except one. This was a 47% efficiency on day nine. The highest daily removal was 99.6% on day twenty-five.

TeCE and TCE levels in the feed stream were found at much lower concentrations than EDC, but showed reactor removal efficiencies near those of EDC. The average reactor efficiency in removing TCE was 73.6% and for TeCE was 77.1%. The calculated stripping rates accounted for 9.4% of TCE removal. Mineralization was presumed to be the only other removal pathway, giving the reactor a biological reduction efficiency of 81.7% for C_2HCl_3. Biological reduction efficiency for each species, i, was calculated from the mass flow rate of species i in the feed stream, the effluent stream and the air stream as:

$$\text{BIOLOGICAL REDUCTION EFFICIENCY} = \frac{\dot{m}_{\text{feed},i} - \dot{m}_{\text{stripped},i} - \dot{m}_{\text{effluent},i}}{\dot{m}_{\text{feed},i} - \dot{m}_{\text{stripped},i}} \times 100 \qquad (1)$$

The reduction efficiency for C_2HCl_3 is given in Figure 5. The best single day TCE removal was 100% on day seven and the poorest daily removal efficiency was 46.6% on day twenty-one. The TCE loading is shown in Figure 6. The average concentration of C_2HCl_3 in the feed was 10.9 mg/L, with the highest loading being 19.1 mg/L and the lowest 2.7.

For TeCE the average reduction was 77.1%. The biological reduction efficiency for TeCE was 64.0% and the stripping rate was calculated to be 19.9%. TeCE removal was consistent at 80% after day ten, but varied significantly before that. On day one the efficiency was 100% dropping to zero on day nine. The TeCE feed rate was an order of magnitude lower than the EDC feed rate. The average TeCE fraction in the feed was 2.5 mg/L with a maximum of 5.3 mg/L and a minimum of zero.

TABLE 1. HENRY'S LAW CONSTANTS USED IN THE STRIPPING CALCULATIONS

Chemical Species	Henry's Law Constant (mm Hg)
EDC	10,302
TCE	141,851
TeCE	172,517

SPECIES IDENTIFICATION

Bacteria were isolated from both the inlet and outlet reactor streams. Though the reactor was initially inoculated with only one species, *Xanthobacter autotrophicus*, five bacterial species were isolated from the effluent stream. Five isolates were found in the groundwater.

Of the five effluent isolates only two have been identified. These are *Xanthobacter autotrophicus* and *Comamonas acidovorans*. *Comamonas acidovorans* was also identified as one of the influent isolates. The three unidentified species from the reactor discharge are thought to have originated in the groundwater.

DISCUSSION AND CONCLUSIONS

An immobilized bed biological reactor was found to effectively remove chlorinated hydrocarbons from contaminated groundwater. The reactor was operated for forty-two consecutive days, treating contaminated groundwater containing three chlorinated hydrocarbons. The reactor showed a very high removal efficiency for ethylene dichloride, the major contaminant in the groundwater. For EDC the average removal efficiency due to biological activity was 90.2%, and the average fraction of EDC in the feed was 226 mg/L.

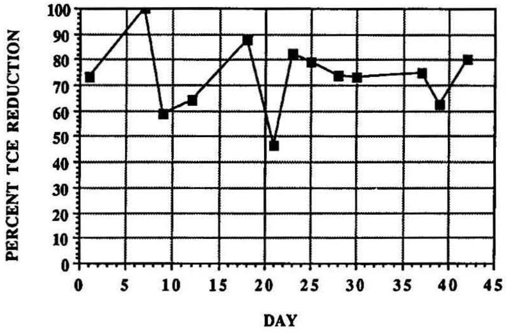

Figure 5. Percent removal of trichlorethylene (TCE) in the reactor.

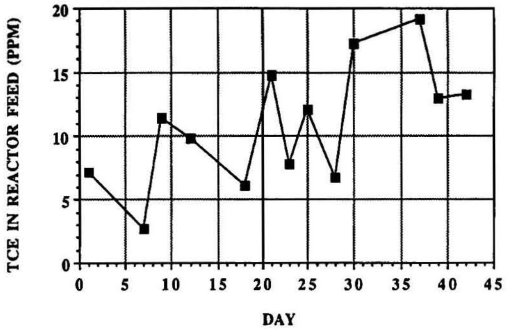

Figure 6. Trichlorethylene (TCE) concentration in the reactor feed stream.

The reactor also demonstrated a good removal efficiency for trichloroethylene and tetrachloroethylene. The average mineralization of TCE in the reactor was 81.7% and the mineralization of TeCE was 64.0%. The average feed of TCE was 10.9 mg/L of the total feed rate, and for TeCE this was 5.8 mg/L (see Figures 7 and 8).

The porous substrate in the reactor bed provided an excellent support for bacterial growth. The bed biomass was stable and effective throughout the test, and the bed proved capable of supporting the large bacterial population required for effective treatment of the groundwater.

The reactor was initially inoculated with only one bacterial species, *Xanthobacter autotrophicus*. However, after initial operation of the reactor it was found that four species from the groundwater were successfully growing in the reactor. The only species that has been identified is *Comamonas acidovorans*.

ACKNOWLEDGMENTS

Institutional research funds from Louisiana State University to support field pilot evaluative studies were provided by the State of Louisiana Board Of Regents Education Trust Fund. Matching corporate support for engineering services and analytical determinations of chlorinated aliphatics was provided by Ethyl Corporation. The daily help and cooperative interest and input by employees of Ethyl Corporation at the North Baton Rouge facility is not only readily acknowledged but deeply appreciated.

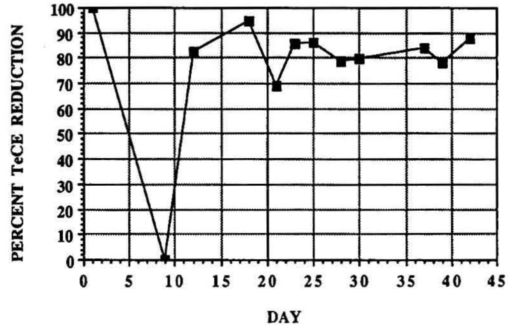

Figure 7. Percent removal of tetrachlorethylene (TeCE) from the reactor feed stream.

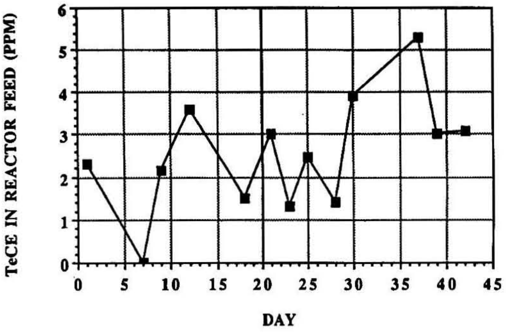

Figure 8. Tetrachlorethylene (TeCE) concentration in the reactor feed stream.

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Cleanup of Contaminated Soils by Pyrolysis in an Indirectly Heated Rotary Kiln

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The destruction of hazardous waste and cleanup of contaminated soils by pyrolysis in an indirectly heated rotary kiln system, followed by combustion of the volatiles in a secondary combustion chamber, has been tested in a pilot plant and demonstrated in an industrial scale plant. Deutsche Babcock Anlagen AG conducted comprehensive tests in a pilot plant with throughput rates of 0.5 to 1 ton/hour. Following these tests, Deutsche Babcock designed and constructed the industrial scale demonstration plant with a throughput rate of 7 tons/hour for Bergbau AG Westfalen near Dortmund, West Germany.

INTRODUCTION

Soils and other materials to be treated are heated in the kiln to 500°C to 650°C, with a maximum temperature of 750°C. The residence time of solids in the kiln is approximately 1 hour. Data from the tests, including destruction efficiencies for various polycyclic aromatic compounds and percent organics remaining in the ash, are presented. In general, the destruction efficiency exceeds 99%.

Operation costs of the system, including maintenance and amortization of capital costs, are between 130 and 160 Deutsche Marks per ton of soil (equivalent: $65-$80 per ton of soil).

Advantages of the system include:

1. Due to the slow warming-up of the material and good mixing, no crust formation occurs during drying. Thus, volatilization of organic constituents is improved.
2. The supply of heat to the indirectly heated kiln can be controlled by heating in sections, giving a higher degree of material temperature control.
3. Lower heat input is required.
4. The gas cleaning equipment can be down-sized.
5. The physical characteristics of the soil are unchanged.
6. No refractory liner is required in pyrolysis kiln.

The solid residue from the indirectly heated kiln is purified to the point where it can be backfilled on the same site.

PILOT-PLANT TEST

Planning for a pilot-plant test of the concept began in 1984 and the tests were completed in 1986. Deutsche Babcock conducted the comprehensive tests in a pilot-plant constructed at the Babcock Krauss Maffei Industrial Equipment Center in Garching, near Munich.

The pilot-plant indirectly heated kiln has a length of 7.20 meters and a diameter of 0.8 meters. Throughput rates near 0.5 ton/hour were tested. Soils and other materials to be treated were heated in the kiln to 500°C to 650°C, with a maximum potential of 750°C. This temperature, combined with the soil residence time of one hour in the kiln, was sufficient to remove 90 to 99+ percent of the highly volatile as well as the most thermally stable substances, such as polycyclic aromatic hydrocarbons.

As may be expected, the destruction efficiency for all compounds tested intensified with increasing treatment temperature and increasing residence time in the kiln.

Operating experience shows destruction efficiencies are consistently above 99 percent. In fact, at a temperature of 650°C (measured by the internal kiln wall), the destruction efficiency was at least 99.9 percent for all compounds tested. And still further increases in destruction efficiency can be achieved by increasing the temperatures up to 750°C, which is possible in the indirectly heated kiln, and/or increasing the residence time of the soil in the rotary kiln.

The high destruction efficiency for an indirectly heated rotary kiln in the decontamination of contaminated soil from the coking plant is demonstrated by the sample results presented in Table 1.

TABLE 1. POLYCYCLIC AROMATIC HYDROCARBONS REMAINING IN THE SOIL AFTER TREATMENT IN THE PILOT PYROLYSIS PLANT

	Rotary Kiln Wall Temperature			
Chemical Compound	350°C	450°C	550°C	650°C
Methyl Naphthalene	7.8	0.5	n.d.	n.d.
Fluoranthene	8.2	0.5	0.2	n.d.
Benzofluoranthene	6	1	n.d.	n.d.
Indenopyrene	2.2	0.6	n.d.	n.d.

concentrations in mg/kg
n.d. = not detectable

The indirectly heated rotary kiln shows the following advantages in comparison with a directly heated system:

- The indirect heat transfer at lower than normal incineration temperatures allows a slower warming-up of the material in the kiln. Therefore, no crust formation occurs and volatilization of all the organic constituents is enhanced.
- The supply of heat to the indirectly heated kiln can be controlled by heating the annular jacket around the kiln in sections; thus the material temperature level and degree of volatilization along the length of the kiln can be easily controlled.
- Considerable savings in heating costs compared to the direct heated kiln system are achieved because lower processing temperatures are required.
- The large amounts of excess air that are typical of direct fired kiln systems are not required for the pyrolysis system. This also saves on the amount of heat that is required to reach the treatment temperature.

BACKGROUND

The cleanup of numerous former waste disposal sites and of soils contaminated by industrial activities is a generally acknowledged necessity. For example, in the United States there are currently 1,173 contaminated sites on the National Priorities list [1]. Additional sites are being added frequently. In West Germany some 48,377 sites are recorded as being possibly contaminated and it is reported that the total number of suspected contaminated sites could rise still further to around 70,000 [2].

As noted, the quantities, contents, structures, and locations of these hazardous wastes and contaminated soils are still being defined but the associated potential dangers for the environment have been made clear by several incidents.

Due to the large variety of chemical and process engineering problems involved, the decontamination of contaminated soils requires a wide range of possible solutions.

One of the more advanced demonstrated solutions is thermal treatment. For this type of treatment, different concepts are possible. Deutsche Babcock Anlagen AG, a company active in nearly all the fields of waste disposal, has developed thermal treatment processes by drawing on extensive experience in a broad range of proven refuse treatment methods including:

- Treatment of industrial wastes in directly heated rotary kilns.
- Fluidized bed combustors for the incineration of homogenous wastes such as sewage sludge, etc.
- Grate systems for the incineration of municipal refuse.
- Pyrolysis plants for the treatment of a broad range of wastes in indirectly heated rotary kilns.

The treatment of wastes in directly heated rotary kilns, fluidized bed combustors, and grate systems has been demonstrated extensively in numerous operating plants. Now Deutsche Babcock Anlagen AG has demonstrated the viability and process advantages of treating contaminated soils and hazardous wastes in an indirectly heated rotary kiln pyrolysis system.

PYROLYSIS CONCEPT

The heart of the pyrolysis process is an indirectly heated rotary kiln. The waste or contaminated soil to be treated is fed into the center of the rotary kiln where it is heated indirectly by firing natural gas in an annular chamber constructed around the rotary kiln shell.

The organic material in the waste decomposes, volatilizes, and is driven into the gas phase by the heat in the rotary kiln. The pyrolysis gas is then combusted to reach the required destruction efficiency in a secondary combustion chamber.

The combusted pyrolysis gas is then scrubbed to remove dust, hydrogen halides, sulfur oxides, and other pollutants before being discharged up the stack and into the atmosphere.

- Further savings are realized by preheating the combustion air by exchanging heat with the hot combusted gases from the annular jacket.
- Since the gases from the annular jacket are not contaminated, they do not require cleaning and can be combined with scrubbed pyrolysis gas in the stack or can be discharged through a separate stack if desired.
- Much larger quantities of flue gas are created in a direct heated rotary kiln. Therefore dust carryover from the direct kiln is considerably higher. The higher dust carryover affects the layout and choice of all downstream components.
- When using the volatilizing process in the indirectly heated rotary kiln, only the organic contaminants are destroyed, while the physical characteristics of the entire amount of inert material remains unchanged. Therefore, soils treated this way can be backfilled.
- Since the directly fired kiln operates at lower temperature, no refractory liner is required. This reduces the capital and maintenance costs. Also, quicker start up and shut down cycles are possible, thereby allowing operation of the system on a "daytime only" basis if desired.

INDUSTRIAL SCALE DEMONSTRATION PLANT

On completion of the successful pilot tests in 1986, an order to construct an industrial scale demonstration plant was placed with Deutsche Babcock Anlagen AG in Krefeld (see Figure 1). Construction and operating permits were granted in June 1987 and construction of the plant soon began. The kiln was commissioned in April 1988. The installation was tested in May and June 1988 by feeding it with contaminated soils. Currently, operations are continuing at the site. The owner of the demonstration plant is Bergbau AG, Westfalen.

Because of its experimental nature, the project receives financial assistance from the Federal Ministry for Re-

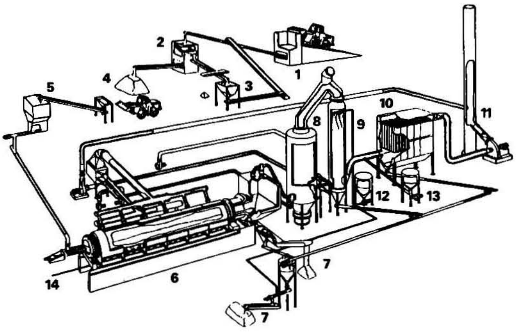

Figure 1. Industrial scale demonstration plant for thermal soil decontamination. Soil preparation: 1. Input 2. Screening 3. Crushing and iron separation 4. Intermediate deposition area. Thermal soil treatment: 5. Soil feed 6. Rotary kiln 7. Soil discharge 8. Pyrolysis gas combustion 9. Flue gas cooling 10. Particulate removal 11. Stack 12. Cooling water 13. Lime 14. Heating gas.

search and Technology. The project sponsor is the Federal Office of the Environment in Berlin. The demonstration plant is located in Unna-Bonen near Dortmund, West Germany, at a former coke oven site.

The industrial scale pilot-plant has a design throughput rate of at least 7 tons/hour with a soil moisture content of 21 percent and 5 percent volatile pollutants.

The soils are contaminated with polycyclic aromatic hydrocarbons such as benzene, toluene, xylene, naphthalene, anthracene, phenols, cresols, and long chain molecules such as paraffins in low concentrations.

The plant features the following components:

- Soil excavation, screening, crushing, iron separation and distribution to the pyrolyzer.
- Feed device.
- Indirectly heated rotary kiln.
- Solid residue discharge device.
- Combustion air preheating by heat recovery exchangers.
- Secondary combustion chamber for pyrolysis gas destruction.
- Flue gas cooler.
- Dry lime injection for neutralizing acid gases.
- Dust separation unit (baghouse filter).
- Induced draft fan and stack.

Figure 2 shows a simplified flow sheet of the plant. The plant works as follows:

Coarse components such as stones, pieces of concrete, and iron are separated from the soil; small parts are crushed to a suitable grain size (smaller than 50 mm) in an impact mill; and iron is extracted by two overhead magnets. After this crushing and preparation, the material is taken to the charging shaft via a trough conveyor. A special wear-resistant twin-screw conveyor is provided for feeding it to the kiln.

The conveyor is designed to always form a sealing plug of feed material so that a suction of 1.5 mbar is maintained in the kiln. The kiln is 21 m long and has a diameter of 2.2 m.

It is heated with hot flue gas produced by 18 natural gas burners installed in the heating jacket. This heating jacket is arranged concentrically around the kiln to provide an even distribution of the flue gas.

A steel plate construction alongside the kiln forms three separate heating zones which are controlled separately. Process conditions can thus quickly be adjusted to the frequent variations of soil moisture. The wall temperature of the kiln, in normal operation, is between 600°C and 650°C.

The exhaust flue gas from the annular heating jacket is taken via headers to a subsequent heat exchanger where the combustion air required within the system is being preheated. Via an induced draft fan, the flue gas is discharged to the stack.

Depending on the physical characteristics of the individual organic compounds, decontamination of the soil is accomplished by volatilizing the low-boiling components and by decomposition of the high-boiling organic compounds.

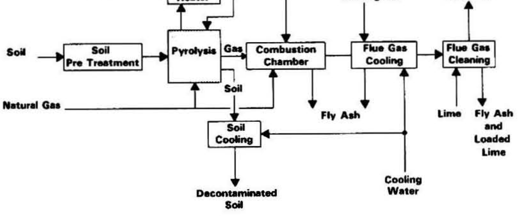

Figure 2. Simplified plant flowsheet for cleanup of contaminated soil by pyrolysis.

The solid residues fall into the discharge chamber. Here a screen screw conveyor separates the soil at 10 mm. The material with grain sizes over 10 mm is fed into a wet deslagger and leaves the plant. The fine material below 10 mm grain size is discharged via a gas-tight system of water-cooled screw conveyors to a discharge silo.

In the conveyors, residues are cooled down below 100°C by water jacketed screws and housings and are then wetted by water sprays to a moisture of about 10 percent so they can be transported and backfilled.

The gaseous organic volatiles and water vapor formed in the kiln are burned in the secondary combustion chamber. Natural gas is provided as auxiliary fuel. The combustion temperature is 1,000°C to 1,300°C, depending on the requirements for complete destruction of the types of organic components present in the soil. The residence time of the pyrolysis gas in the combustion chamber is approximately 3 seconds.

In the subsequent cooler, flue gas from this combustion chamber is cooled down to approximately 180°C by water spray/quench and thus prepared for optimum gas cleaning. Dust is separated from the flue gas in a baghouse filter. Hydrogen halide and sulfur oxide emissions are controlled in the pyrolysis kiln by the addition of lime with the waste. However, should admissible limits of sulfur oxides and hydrogen halides be exceeded, lime addition facilities are installed upstream of the baghouse filter.

At a minimum temperature of 120°C and a maximum of 180°C, flue gas is discharged via an induced draft fan to the stack.

The process design and sizing of the industrial scale demonstration plant is as shown in Table 2:

RESULTS

In the first industrial scale thermal soil decontamination plant, approximately 35,000 tons of soil have been

TABLE 2. PROCESS DESIGN AND SIZING OF THE INDUSTRIAL SCALE DEMONSTRATION PLANT

Soil Feed	
Volume	7000 kg/hr
Moisture	21%
Inerts	69%
Volatiles	5%
Carbon	5%
Grain Size	<50 mm
Rotary Kiln	
Diameter	2.2 m
Length	21 m
Heating Effic. max.	12.6 GJ/h
Pyrolysis Temp	750°C
Lining	None
Secondary Combustion Chamber	
Reactor Temp.	1300°C
Heating Effic. max.	10.5 GJ/h
Flue Gas Volume	6020 cu m/h (STP)
Air Heater	
Flue Gas Volume	7800 cu m/h (STP)
Flue Gas Temp. in/out	700/300°C
Air Volume	4400 cu m/h (STP)
Air Temp. in/out	10/350°C
Flue Gas Cooler	
Flue Gas Volume inlet	10020 cu m/h (STP)
Flue Gas Volume outlet	14550 cu m/h (STP)
Flue Gas Treatment	
Glue Gas Volume inlet	14550 cu m/h (STP)
Flue Gas Temp. inlet	190°C

TABLE 3. TEST RESULTS, KÖNIGSBORN PLANT

Date	March 8, 1989		January 27, 1989	
Pollutant	Input mg/kg	Output mg/kg	Input mg/kg	Output mg/kg
Naphthalene	101.00	1.7	161.60	0.5
2-methyl-naphthaline	40.20	0.5	73.80	0.1
1-methyl-naphthaline	23.40	0.3	42.90	0.1
Dimethylnaphthaline e	n.d.*	n.d.	93.20	0.3
Acenaphtylene	n.d.	n.d.	68.20	0.1
Acenaphthene	n.d.	n.d.	42,30	0.1
Fluorene	156.00	0.1	238.00	0.1
Phenantrene	686.00	0.6	1055.30	1.4
Anthracene	281.00	0.1	226.00	0.3
Fluoranthene	n.d.	n.d.	688.60	1.3
Pyrene	236.00	0.1	398.20	0.6
Benzo(a)anthracene	155.00	0.2	2259.20	0.3
Chrysene	214.00	0.5	134.60	0.9
Benzo(e)pyrene	66.60	0.4	111.50	1.1
Benzo(b)fluoranthene	112.00	0.1	168.50	5.2
Benzo(k)fluoranthene	43.70	0.1	81.90	0.3
Benzo(a)pyrene	86.60	0.2	138.10	0.4
Dibenzo(ah)anthracene	16.80	0.1	23.20	0.1
Benzo(ghi)perylene	14.00	0.1	60.20	0.1
Indeno(1.2.3.cd)pyrene	33.80	0.1	69.50	0.1
Sum	2266.10	5.2	6134.80	13.4
Decontamination efficiency in %		99.77		99.78

n.d. = not detectable

treated in the past eighteen months in two 8-hour shifts daily, and since August 1989 it has been in continuous operation 5 days a week.

Today, the destruction of 17 different polycyclic aromatics has been measured. The sample results, presented in Table 3, confirm the experiences of the pilot-plant tests. More than 99 percent decontamination efficiency has been reached.

The dust residues from flue gas cleaning have approximately the same chemical composition as those of the treated soils from the low temperature indirectly heated kiln, so they can be backfilled together.

The concentration of noxious gas components in the flue gas from the system is measured continuously. Lime is fed to the kiln with the soils, and in the gas cleaning system to keep noxious gas concentrations below permitted levels.

TABLE 4. STACK GAS POLLUTANT CONCENTRATIONS

Pollutant Compound	Permitted Concentration* mg/cu m	Measured Max. Values* (half hourly mean values) mg/cu m
Dust, fine particulate	<30	24
Carbon monoxide	<100	60
Hydrogen Chloride	<50	15
Hydrogen fluoride	<2	0.6
Sulfur dioxide	<100	70
Nitrogen oxides (NO_x as NO_2)	<500	275

*Concentrations are based on dry gas at 11 Vol. % oxygen, 0°C, 1013 Pa.

TABLE 5. OPERATING COSTS PER TON OF THERMALLY TREATED SOIL

Cost Item		Costs D-Marks/ton
Capital Costs		33-40
6,000 hours/year		
10-Year Depreciation		
15% Interest		
Operating Costs		70-80
Heating		
Natural Gas		
Water		
Electricity		
Lubrication		
Lime		
Maintenance	(2% of Capital Costs)	
Insurance	(0.5% of Capital Costs)	
Personnel Costs		23-43
Total Operating Costs		130-160

The pollutant concentrations in the flue gas leaving the stack are as shown in Table 4.

COSTS

The capital cost of the industrial scale plant is approximately 11 million West German marks (5.5 million equivalent U.S. dollars).

Operation costs for thermal treatment in the industrial scale plant are estimated at between 130 and 160 West German marks (65 and 80 equivalent U.S. dollars) per ton of soil, depending on the daily operating period. Amortization of the plant capital costs, personnel costs, maintenance, and insurance costs are all included in this estimate as shown in Table 5. The cost of excavation, prefeed treatment and backfilling are dependent on the conditions in the contaminated area. They can vary over a wide range.

CONCLUSION

The tests with the industrial scale thermal soil decontamination plant have shown that the treatment of organically contaminated soils in an indirectly heated rotary kiln is not only feasible but offers many potential process and cost saving advantages over thermal treatment in a directly fired kiln.

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Performance of Selected *In Situ* Soil Decontamination Technologies: An Air Force Perspective

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Every year, the U.S. Air Force stores and transfers three billion gallons of JP-4 jet fuel. Unfortunately, not every gallon of fuel has been consumed in flight. Fuel spills account for nearly half of the chemically contaminated sites on Air Force installations and that percentage is growing as underground storage systems are more closely inspected. The Air Force Engineering and Services Laboratory is responsible for developing and testing new and more cost effective technologies capable of cleaning up fuel spills in a variety of soil and groundwater conditions. Special emphasis has been placed on soil decontamination because our sampling data has confirmed that the majority of spilled fuel is adsorbed or occluded in the soil above the water table.

INTRODUCTION

This paper summarizes the results of several field tests which have used a variety of *in situ* technologies to treat soil contamination. Observations on the success and shortfalls of *in situ* soils washing, enhanced biodegradation, soil venting and radio-frequency soil heating are presented in an abbreviated format. These field tests have shown that *in situ* decontamination methods which use water as a contact medium to remove hydrocarbons from the vadose zone have consistently fallen short of their cleanup goals. Technologies which use vented air and thermally enhanced venting for contacting fuel residuals in the soils have met with greater success. These results indicate that the physical accessibility of fuel residuals to treatment media is critical to the success or failure of soil decontamination technologies.

LIMITED ACCESS

During the past two decades, researchers have primarily focused on discovering and optimizing chemical and biological reactions which will alter or degrade fuel hydrocarbons with little regard for the engineering of effective application systems. Using batch and column experiments, laboratory success has been achieved in biological degradation [*1*], surfactant soils washing [2], and chemical oxidation [3]. However, field testing has shown that contact between injected or infiltrated treatment chemicals and hydrocarbon contaminants is very difficult to achieve. Soil structure, fuel composition, and the depth at which the release of fuels occurred are just a few of the factors affecting accessibility that should be examined prior to selecting any *in situ* technology.

Low permeability silts and clays slowly accept fuel hydrocarbons into their available pore space. This can retard the advance of fuel spills, but it results in a highly inaccessible fuel residual. Fuels become trapped in soil micropores and form a thin film over the large surface area of these fine-grained materials. Water attempting to convey a chemical or biological treatment media to these fuels is limited both by a low hydraulic permeability and channeling through larger pore spaces. Even in larger-grained sandy soils, fuel blobs can become trapped in pore throats and in small pores, causing water to channel through only the large, unblocked pore spaces [*4*].

The type of fuel also impacts accessibility for treatment. The viscosity, solubility and bulk vapor pressure are important factors in predicting fuel residual accessibility and response to water or air contact. For example, gasoline typically contains a greater fraction of water soluble compounds and has a higher bulk vapor pressure than jet fuels. As a result, gasoline is very accessible to water- and air-based treatment methods. Less viscous diesel and heating fuels are more likely to completely fill available pore spaces and retard the advancement of treatment media. Accessibility is also limited by the lower vapor pressure and water solubility of heavier fuels.

The location of the initial fuel release relative to the water table and capillary fringe also effects the distribution of fuel residuals in soils. Laboratory experiments indicate that when hydrocarbons are released in water-saturated or near-saturated conditions, they form large blobs which are trapped in larger pore spaces with little displacement of water from micropores. However, fuels released in drier soils above the water table tended to migrate into micropores and form thin films over soil particles [5]. These residuals may have more limited contact with treatment fluids. Our field experiments have clearly shown that fuel accessibility, and the factors which determine fuel location in the soil matrix, deserve far more attention by both the scientific and engineering community.

In the early 1980s the EPA Hazardous Waste and Engineering Research Laboratory at Edison, New Jersey performed experiments using a variety of surfactant solutions to remove crude oils and PCBs from contaminated soil columns [6]. The results of these column tests showed that after passing ten pore volumes of a 4 percent surfactant solution through the columns, 86 percent of the crude oil and 98 percent of the PCBs were washed from the soils. With these promising results, the EPA and AFESC initiated a joint project to pilot test *in situ* soils washing at a contaminated Air Force site.

Because soils washing is best suited for permeable soils, a sandy site was desirable. An abandoned fire training area at Volk Field Air National Guard Base (ANGB) in Wisconsin was selected as a research site. Historical data [7] indicated that the fire training area had been used since 1955 and that as much as 200,000 liters of JP-4, waste oils and solvents may have soaked into the soils.

A sieve analysis of the soil confirmed a uniform sand with less than 5 percent fines by weight. The soil was unconsolidated to a depth of 3 to 5 meters where a highly compacted sandstone was encountered. The vertical permeability of the soil in the unsaturated zone was measured in a laboratory permeameter at 4×10^{-3} to 5×10^{-4} cm/sec. The hydraulic properties of this soil seemed acceptable for a soils washing application.

A series of *in situ* test beds, each containing 0.2 m^3 of undisturbed soil, was established in the fire training area and initial soil samples were taken to establish baseline contaminant levels. Soils were analyzed using two methods, an oil and grease extraction was used as a general indicator of hydrocarbon contamination, and a gas chromatograph was used to analyze the volatile aromatic and aliphatic fractions of the fuel. Initial oil and grease values ranged from 1000 to 6000 mg/kg of soil.

Three synthetic surfactant solutions mixed in clean water were used in this field test and recirculated groundwater was used as a control. Wash solutions were applied at the rate of 70 liters/m^3/day for six consecutive days. An unexpected decrease in percolation rate was observed in all of the test beds. After 14 pore volumes were passed through the soil, the test beds were rinsed with clean groundwater to remove excess surfactants. The test beds were then resampled to determine contaminant removal rates.

Soil samples were collected from two depths (5-10 cm and 30-35 cm below the surface) in each test bed. These samples were again analyzed for oil and grease. The results of the post-test analysis showed that surfactant solutions did not provide a statistically significant decrease in fuel and oil contamination at either depth. Despite the repeated success of engineered surfactants to clean contaminated soils in laboratory columns, the sandy soil at the Volk Field site was not cleaned *in situ*. Within statistical limits, there was no significant difference in pre- and post-wash contaminant levels.

Although the laboratory columns were packed to simulate *in situ* soil density and permeability, the reduction in permeability and incomplete contact with fuel residuals encountered in the field test was not predicted in the laboratory. This underscores the importance of pilot testing on contaminated sites before committing to full-scale decontamination technologies.

ENHANCED *IN SITU* BIODEGRADATION

Common soil microorganisms have the ability to degrade virtually all of the hydrocarbons found in common fuels. Many scientists [8, 9] have confirmed fuel biodegradation under favorable aerobic conditions. Enhanced *in situ* biodegradation is an attempt to create these favorable aerobic conditions in an environment of heterogeneous soils and delicate geochemical balances. While several commercial firms have claimed successful site remediations, published results often lack sufficient data to determine the effectiveness of biodegradation in reducing fuel residuals in the soil. For this and other reasons, our laboratory decided to conduct independent field tests of this technology prior to recommending it for widespread Air Force application.

In 1984, our laboratory initiated a pilot-scale test of enhanced biodegradation at a site on Kelly AFB, TX [*10*]. As this test progressed, problems with soil permeability were encountered reducing the delivery of hydrogen peroxide and nutrients through injection wells. This reduction in permeability was attributed to both natural silt and clay soils and the precipitation of calcium phosphates which formed as injected phosphates reacted with calcium in the soil. Permeability problems reduced the delivery of oxygen and consequently little biodegradation occurred. Based on these results a second site was selected at Eglin AFB, FL for additional testing under more favorable hydraulic conditions.

In 1984 a fuel leak was discovered in a 15 cm (6 in.) underground JP-4 fuel supply line inside the base fuel storage compound on Eglin AFB. At the time of discovery, an estimated 75,000 to 100,000 liters of fuel had contaminated over 3000 m^3 of soil and shallow groundwater. A series of shallow, gravel filled trenches and skimmer pumps were used to recover over 30,000 liters of fuel. In 1986, we initiated a field test of enhanced *in situ* biodegradation. The site is located in an area of unconsolidated coastal sands that extend from the surface down to 12 meters where a thick layer of clay is encountered. Groundwater is found only one meter below the surface and has a high hydraulic conductivity of 6×10^{-2} cm/sec. These favorable soil and hydraulic properties made it an excellent site for testing enhanced biodegradation.

Extensive soil and groundwater sampling preceded the test. Soil samples were taken from 4 to 6 in. depth intervals at 12 sampling locations across the site and analyzed for total petroleum hydrocarbons using EPA Method 418.1. Soil and groundwater samples from four of the locations were analyzed using a GC/MS and 43 representative compounds were identified for special monitoring. Site characterization confirmed that over 90 percent of the jet fuel remaining on the site was above the water table, adsorbed and occluded in the soil matrix. Although the leak occurred at or slightly below the water table, rising and falling ground water had deposited hydrocarbons across a one meter profile.

A nutrient and hydrogen peroxide delivery system was designed to test the relative effectiveness of three delivery methods in stimulating biodegradation in the vadose zone and in the groundwater. Two shallow injection wells, infiltration galleries and a spray irrigation system were all installed for a side-by-side comparison. Four downgradient recovery wells were installed and initially produced 150 to 190 liters/min (40 to 50 gpm) for recirculation through the site. Due to the presence of 10 mg/l of iron in the shallow groundwater, an aeration basin and settling tank were added to precipitate and remove iron prior to reinjection. Iron fouling is a common cause of reduced permeability and failure of reinjection systems.

Several important tests were completed in advance of full-scale operation which began in June of 1987. Prior to nutrient/peroxide additions, site hydrology was studied under pumping and delivery conditions. The initial capacity of the three delivery systems was measured to provide a baseline for site permeability. A conservative chloride tracer was introduced into the infiltration gallery and its transport monitored across the well field to ensure hydraulic connection across the site.

Fuel contaminated soil and groundwater were observed in laboratory microcosm studies to determine the general activity of existing fuel degrading microorganisms and their response to nutrient and oxygen additions. Simple bench-scale microcosm studies confirmed that under enriched oxygen and nutrient conditions, existing soil bacteria could degrade soluble, aromatic hydrocarbons in less than two weeks. Unfortunately, success is not measured in laboratory flasks but in the field where these optimum conditions are much more difficult to achieve.

Oxygen supply and distribution is absolutely critical to field success. Although estimates vary, complete biodegradation of fuel compounds will require 2 to 3 grams of oxygen per gram of fuel degraded. An interesting discussion on the importance of the oxygen requirement is found in a recent publication by Hinchee [*11*].

Hydrogen peroxide is the most frequently used oxygen source for enhanced biodegradation. Peroxide is capable of releasing enough oxygen to saturate injected groundwater to its oxygen solubility limit of approximately 40 mg/L. This is a substantial improvement over the 10 mg/l O_2 solubility for standard aeration of groundwater. However, hydrogen peroxide is inherently unstable and its use depends upon a gradual breakdown of peroxide and time release of oxygen downgradient of injection points.

Shortly after initiating 500 ppm hydrogen peroxide additions at the Eglin site, gas bubbles were noticed coming up through the water in the shallow infiltration galleries. Gas sampling showed that this was virtually pure oxygen; the product of rapid peroxide decomposition. Iron was first suspected as the catalyst of this rapid decomposition. However, laboratory tests showed that the rate of H_2O_2 decomposition in iron solutions was at least an order of magnitude slower than field decomposition rates. Subsequent laboratory experiments by Spain [*12*] found that peroxidase enzymes produced by indigenous bacteria were the cause of uncontrolled H_2O_2 decomposition. As a result of this oxygen off gassing, only an estimated 16 percent of the potential oxygen supply was actually delivered to the contaminated soil and groundwater. Although there was a slight increase in dissolved oxygen levels downgradient of injection points, there was no evidence of H_2O_2 transport.

After 18 months of peroxide and nutrient additions, aromatic concentrations in groundwater monitoring wells had decreased from 8 ppm to 200 ppb. However, intense sampling of soils above and beneath the water table did not show a significant removal of soil-bound fuel residuals [*13*]. The failure of nutrient and hydrogen peroxide additions to impact soil contamination was particularly evident in the unsaturated zone of the spray application area. Over 190 pore volumes of treatment water passed through these sandy soils with no significant fuel removal measured. It appears that neither hydraulic washing nor biodegradation had an impact on this tightly bound fuel residual. We have concluded that fuels trapped within the micropores of the soil were largely inaccessible to the nutrients and oxygen that were being provided.

Our experiences at Kelly AFB and Eglin AFB test sites have shown that enhanced biodegradation cannot be applied at sites with poor permeability and that contaminant accessibility can be a problem even in more permeable, sandy soils. This technology seems best suited for sandy or gravel aquifers where the majority of the contamination is in the saturated zone. A similar test of this technology conducted by the EPA's R. S. Kerr Laboratory showed some improvement in hydrogen peroxide stability, particularly when the hydrogen peroxide was injected into the saturated zone [*14*]. *In situ* peroxide stability is clearly a major design consideration that should be determined through a carefully monitored pilot test on each site. If the potential oxygen concentration achieved with hydrogen peroxide is not substantially greater than the 40 mg/l available through pure oxygen aeration, then the use of hydrogen peroxide is not cost effective.

IN SITU SOIL VENTING

In situ soil venting is a soil decontamination technique which uses vacuum blowers to pull large volumes of air through contaminated soil. The air flow sweeps out the soil gas, disrupting the equilibrium existing between the contaminants on the soil and in the soil vapor. This causes volatilization of the contaminant and subsequent removal in the air stream. *In situ* soil venting has reportedly been successful for removal of volatile contaminants such as gasoline [*15*] and trichloroethylene [*16*].

Because of the reported success of the technology on volatile contaminants in soils, the Air Force Engineering and Services Laboratory began a research project with Oak Ridge National Laboratory to conduct a full-scale test of *in situ* soil venting at a jet fuel (JP-4) spill site. In general, JP-4 has more heavy molecular weight hydrocarbons and is less volatile than gasoline and other contaminants which have previously been investigated for remediation by *in situ* soil venting.

The site chosen for test was in a fuel yard at Hill AFB, UT where a 100,000 liter JP-4 spill had occurred in January 1985. The JP-4 spill site is in an area of medium to fine dry sands with thin interbedded layers of silty clay. This soil type extends to a depth of approximately 180 meters below land surface. Perched groundwater had been encountered on top of the silty clay layers. The regional aquifer of greatest significance as a water bearing unit is at an average depth of 180 meters. After extensive soil sampling and multiple soil gas surveys, it was determined that the spill had contaminated an area 37 meters by 37 meters to a depth of approximately 15 meters below land surface.

Information from the site characterization and the one-vent pilot test [*18*] provided the basis for the design of a full-scale *in situ* soil venting system for remediation of the JP-4 contaminated soil. The full-scale venting system design consisted of the three subsystems: 1) A vertical vent array in the area of the spill, 2) A lateral vent system under a new concrete pad for the recently excavated underground storage tanks (USTs) and 3) A lateral vent system in the pile of soil from the excavation of the USTs. This design includes features which permit evaluation of several factors affecting contaminant transport and subsurface air flow.

The vertical vent subsystem consists of 15 vents placed in the contaminated area to depths of 15 meters. The venting subsystem under the new concrete pad includes six lateral vents spaced 46 meters apart at a depth of approximately 6 meters below land surface. The subsystem for the excavated soil pile consists of eight vents spaced 5.5 meters apart at a depth of 1.5 meters below the top of the pile. This pile is approximately 49 meters long, 13 meters wide, and 4 meters high. A blower/emission control system was installed for inducing air flow to the three subsystems and for treating emissions as necessary to meet regulatory requirements. A condensation drum, flowmeters, and gas monitors were also included in the system.

Operation of the full-scale, *in situ* soil venting system began in December 1988. As of October 1, 1989, approximately 50,000 kilograms of JP-4 hydrocarbons have been extracted in the vented soil gas. Decontamination of the site can be seen by comparison of soil gas concentrations in an area of the vertical vent system. The highest soil gas hydrocarbon concentrations have dropped from 179 percent of the lower explosion limit (LEL) in February 1989, to 88 percent LEL in April 1989, to 33 percent LEL in June 1989, to 5 percent LEL in August 1989. Also, the concentration of hydrocarbons in extracted gas from the entire venting system has dropped from 38,000 ppm hexane equivalent in December 1988 to 500 ppm hexane equivalent in October 1989. This is below the level required for mandatory site cleanup in some states (*e.g.*, Florida [*18*]). The state of Utah has not set standards for cleanup levels of petroleum contaminated soils.

Another important mechanism of remediation from *in situ* soil venting, besides volatilization and removal, is biodegradation. The increased oxygen levels in the soil gas due to infiltration of atmospheric air may considerably stimulate biological activity. To evaluate this factor, carbon dioxide and oxygen are being measured in the extracted gas at the soil venting test. Initially, high CO_2 (11%) and low oxygen (1%) levels were measured in the soil gas. As venting continued, the CO_2 levels decreased and the oxygen levels increased. Carbon dioxide levels have continued to be an order of magnitude higher than atmospheric, which suggests biodegradation may play a significant roll in the remediation of the site.

The results obtained to date from the JP-4 *in situ* soil venting test have shown that this technique is very effective in removing large amounts of jet fuel from the soil in a relatively short period of time. Continued testing is aimed at determining the importance of various factors in hydrocarbon removal. We are continuing to sample the extracted gas to determine both the total hydrocarbon levels and hydrocarbon distribution. The effects of moisture on volatilization and bioactivity will be determined by monitoring soil moisture and extracted gas humidity. In October 1989, the system was shut down for an extensive soil sampling to determine the extent of the JP-4 hydrocarbon removal. Based on the data from the extracted gas, we project that 70 to 80 percent of the 100,000-liter spill will have been removed by the time of the sampling. Final data from this site will provide a valuable tool for full-scale design of *in situ* venting systems for JP-4 and other fuel contaminated sites.

RADIO-FREQUENCY THERMAL SOIL DECONTAMINATION

In 1985, the Air Force Engineering and Services Laboratory and the Environmental Protection Agency began a joint research project with the Illinois Institute of Technology Research Institute (IITRI) to explore the use of radio-frequency (RF) heating for *in situ* soil decontamination. Radio-frequency heating uses electromagnetic energy directed through electrodes in the soil to create molecular vibration and rotation, which uniformly heats the soil. Radio-frequency heating was first developed for recovering oil from oil shale and tar sands in the 1970s. Field tests proved the feasibility of heating rock formations from 200°C to 400°C. As the energy crisis calmed, IITRI sought out alternative applications for *in situ* soil heating. Because most Air Force contaminants, including JP-4 fuels, have boiling points less than 150°C, RF heating was seen as having great potential for soils decontamination on Air Force installations.

Laboratory experiments, using soils contaminated with fuels and solvents, produced excellent results, with over 95 percent removal at temperatures of 100°C to 150°C. Follow-on experiments in 5 foot soil columns proved the feasibility of uniformly removing volatilized hydrocarbons over the depth profile. These promising results led to a decision to conduct a pilot test of this technology at a contaminated Air Force site.

The abandoned fire training area at Volk Field ANGB, WI was selected as a test site because of its uniform soil and contaminant profile. Although a description of the site is contained in the soils washing section, it is important to point out that a great deal of additional soil sampling was performed for this test to study the removal of different compounds at different depths in the treatment volume. Over 84 different soil samples were obtained from three depths within the 500 ft^3 test volume.

A trailer-mounted 40 kw RF generator was available from past DOE research and was transported to the test site. The test volume measured 4 meters long, 2 meters wide and 2 meters deep and was heated by 39 electrodes in 3 rows of 13 each. A vapor barrier was placed over the heated area to collect escaping soil gas and to transport the gas to a vapor condenser for separating liquid hydrocarbons, and a carbon bed to treat remaining volatile organics. A 560 liter/min (20 cfm) vacuum provided a slight negative pressure to ensure that all vapors were collected and treated. The test volume and gas handling system was heavily instrumented to provide soil temperature data and hydrocarbon concentration data in the escaping gas stream.

RF energy was applied to the soil over a period of 12 days. After 8 days the 150°C target temperature was achieved throughout the test volume and this temperature was maintained for a period of 4 more days. During this heating period, careful records were kept on the release of hydrocarbons and water vapor from the soil. At one point an inert tracer was injected into the soil outside of the treatment area to confirm that migration was into the heated zone and to estimate soil gas velocity. Power consumption was also monitored to determine the operating cost of this process. After 12 days, power was turned off and the soil was allowed to cool prior to resampling.

The efficiency of the RF decontamination process was determined by Dev, *et al.* [*19*] through a careful comparison of pretest and posttest soil samples. Samples were analyzed to determine changes in moisture, volatile aliphatics, volatile aromatics, and semivolatile aliphatics and aromatics. The average removal rates from the heated volume were impressive with 97 percent removal of semivolatile hydrocarbons and 99 percent removal of volatile aromatics and aliphatics. Closer examination of the samples showed that contaminant removal at the 6-foot depth, the fringe of the heated zone, exceeded 95 percent. The total RF process consumed approximately 800 kw-hr/yd^3. Use of a state-of-the-art RF generator for full-scale applications could reduce the power input to less than 500 kw-hr/yd^3.

FUTURE RESEARCH

Future research conducted by the Air Force Engineering and Services Laboratory will emphasize new applications of the soil venting process to remove or destroy fuel residuals in the unsaturated zone. The demonstrated ability of air to access soil-bound fuel residuals represents a distinct advantage over water based treatment systems. Although the authors' conclusions are based primarily on personal field experiences, we have found no convincing evidence in open literature to suggest that *in situ* water based treatment has consistently remediated fuel contaminated soils.

Two enhancements to the soil venting process will be developed and tested during the next year. One enhancement is the combination of soil venting and RF heating to more rapidly volatilize fuel residuals and to increase the volatilization of compounds with higher boiling points. The uniform heating provided by radio-frequency energy is also expected to improve soil porosity and improve removal rates in clay and silt soils. A full-scale test of the RF heating/venting system will be conducted on an Air Force site in 1990-1991.

A second enhancement of the soil venting process will attempt to optimize the biodegradation of fuels that results when vented air provides oxygen to subsurface bacteria. The goal of this research will be to determine the optimum range of soil moisture, nutrients, and venting rates to achieve *in situ* biodegradation while minimizing the emission of volatile organics to the atmosphere. A pilot-scale test of this enhanced biodegradation method is now underway at a fuel contaminated site on Tyndall AFB, FL and is producing encouraging results.

Research is continuing in the use of *in situ* and aboveground biological, physical and chemical treatment technologies to remediate contaminated groundwaters. Because site remediation will generally require two or more technologies, more emphasis will be given to systems integration to impact both source and dispersed contaminants at minimum expense.

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Innovative Management of an Aerated/Facultative Lagoon Suspended–Growth Biological Treatment System for High Strength Industrial Waste Stabilization

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Coors BioTechnology Products Company, in Johnstown, CO is a subsidiary company of Adolph Coors Brewery Company in Golden, CO. Coors BioTech is a corn wet–milling industrial plant which processes shelled corn and converts it into several basic economical products: high fructose corn syrup (HFCS), corn oils, starch, sugars, and various agricultural by–products (Figure 1). The corn wet–milling operation and HFCS refining process generates a continual discharge of numerous process wastes. This wastewater is characterized as being a high strength, soluble, biodegradable waste, highly variable in composition. Coors BioTech treats their own industrial waste on site at their wastewater treatment plant using the activated sludge process. The objective of this paper is to provide a more complete understanding of the necessity for innovative management of the Aerated/Facultative Lagoon in the Coors BioTech waste treatment process, and suggest the applications of such lagoons in secondary biological treatment systems for high strength industrial waste stabilization [*1-5*].

INTRODUCTION

The Coors BioTech industrial waste stabilization process primarily consists of two efficient biological treatment systems: a 31,800 m^3 (8.4 MG) Aerated/Facultative Lagoon system and a 23,500 m^3 (6.2 MG) conventional activated sludge system (Aeration Basin), complete with flow and strength equalization basin, chemical/nutrient blend tank, sludge reaeration, sludge return or waste (sedimentation basin), and settling pond (Figure 2). Combined effluent from the second–stage settling pond and first–stage sedimentation basin is disinfected with chlorine and discharged to the Little Thompson River. The excellent treatment efficiency of high strength industrial waste stabilization experienced at this wastewater treatment facility is derived from the innovative management of the Aerated/Facultative Lagoon treatment process and its unique operation, performance, and process stream flexibility. Overall, the activated sludge waste treatment plant maintains an efficiency in excess of 96% BOD reduction and 92% SS removal, as well as compliance with all NPDES discharge permit limits.

Research objectives were accomplished by a twelve–month full–scale plant study from May 1986 to May 1987 and a six–month bench–scale pilot–plant study from December 1986 to May 1987. An examination of the kinetics of biological suspended–growth provided valuable insight and understanding of the high performance, unique capabilities, and innovative operating strategies of the Aerated/Facultative Lagoon at Coors BioTech. The kinetic study was accomplished by examining bio–oxidation in the Lagoon with the use of a bench–scale (8.5 liter) pilot–plant. It was designed to simulate the physical, chemical, and biological environments of the full–scale 8.4 million gallon (MG) operating Lagoon treatment system. Discussion of the kinetic study and results of the biological growth rate modeling can be found elsewhere [6].

Research results of the performance and innovative management of an aerated/facultative lagoon suspended–

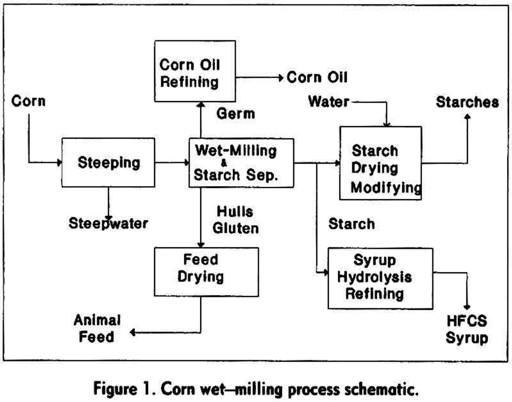

Figure 1. Corn wet–milling process schematic.

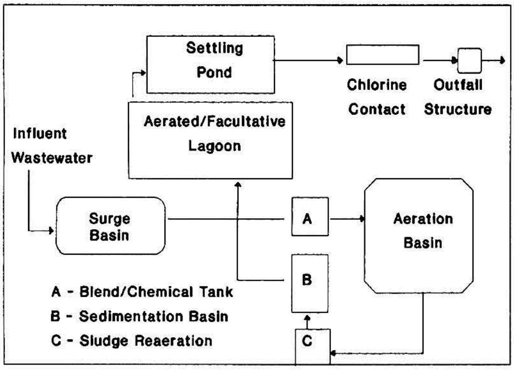

Figure 2. Original process flow schematic.

growth biological treatment system are presented to suggest the importance and applications of such treatment processes as a viable alternative for high strength industrial waste stabilization.

BACKGROUND

Wastewater Characteristics

The corn wet–milling operation generates a continuous waste discharge, variable in composition at a volume of approximately 757 m^3/d (0-20 mgd). The total volume of process wastewater requiring treatment during the study was approximately 268,700 m^3/yr (71 MG/yr). Non–contact cooling waters usually treated in an adjacent spray–pond system were intermittently discharged to the waste treatment plant. Domestic wastes were discharged to the local town wastewater treatment plant (POTW). While 757 m^3/d (0.20 mgd) of wastewater can be considered low or moderate, its average biochemical oxygen demand (BOD) concentration of 4400 mg/L and total dissolved solids (TDS) concentration of 13,200 mg/L is characterized as a high strength organic waste. Typical influent wastes can vary widely in a period of minutes: flow (3-38 L/s or 50-600 gpm); pH (1.0-12.0 s.u.); sugar content (0-20%); BOD (2000-18,000 mg/L); COD (2400-21,600 mg/L), suspended solids (10-2300 mg/L); ammonia (30-1000 mg/L); phosphorus (40-160 mg/L); and sulfides (10-100 mg/L).

Major process wastes at Coors BioTech originate from steepwater evaporators; starch modifying, washing, dewatering, and drying; syrup refining through cooling, activated carbon treatment, column regeneration, and ion exchange regeneration; chemical batching and regeneration; syrup evaporation, storage, and shipping [7]. These process waste sources generated daily wastes which included high–fructose corn syrup, modified starches, light and heavy steepwater, gluten, carbon, chemical regenerates, ammonia, sulfur, acids, caustic, solvents, and biocides. The corn wet–milling and HFCS refining process uses sulfur dioxide to "crack" the corn, ammonia to refine the syrup, and phosphorus–rich agricultural ditch water for general plant process cooling water. These chemicals significantly contributed to the contaminant load and required stabilization and treatment, prior to discharge, to meet permit limits.

The industrial wastewater was primarily comprised of soluble carbohydrates. The total organic waste load to the waste treatment plant averaged 4.7 kg/m^3 (19.5 tons BOD/MG) or 3450 kg/d (7800 lbs BOD/day). Very little waste was particulate or colloidal solid material. This did not allow for easy pollutant removal through screening, sedimentation, or filtration processes. Rather, a biological and chemical treatment system was needed to treat the industrial wastewater discharged from Coors BioTech's corn wet–milling and syrup refining processes.

Treatment System Design

The original design of the treatment plant was operated in a series flow pattern; Surge/Equalization Basin to Aeration Basin (first-stage) to Aerated Lagoon (second-stage) to Settling Pond to final discharge (Figure 2) [8]. The process flow described was designed and constructed in the spring of 1984 as a "bare bones" plant with the objective to provide a functional facility with sufficient capacity to handle a diverse and dynamic waste stream from the corn wet–milling operation and meet NPDES requirements. A projected life of 2 to 5 years was given for this original design, with the anticipation that future wastewater quantities and contaminate loads as a result of increased corn grind production, would necessitate improvements to meet the waste treatment demands.

The wastewater treatment plant has demonstrated its unique ability to easily change and alter the original process flow design to handle increased loads and achieve higher waste removal rates, optimize plant treatment capabilities, and control various operational/process upsets. Figure 3 shows the diverse stream flow capabilities of the Aerated/Facultative Lagoon System, which have allowed unique configurations to be developed and innovative operating strategies to be implemented for successful treatment of the high strength industrial waste. Utilizing these resources has achieved effluent quality which met the stipulated NPDES permit waste load limits for all months in treatment plant existence. The plant has produced extremely clean final effluent of less than 10 mg/L as TSS and BOD, from influent wastes in excess of 2000 mg/L in TSS and 10,000 mg/L in BOD, during periods of maximum performance.

FULL–SCALE LAGOON RESEARCH APPROACH

Operational Modes

To qualitatively and quantitatively define and understand the Aerated Lagoon's impact in the overall waste treatment process, its performance and treatment capabilities were studied as a function of specific physical, chemical, and microbiological properties; material balances; operational conditions; aquatic environments; and treatment problems [9]. Throughout the study, innovative uses of the Aerated Lagoon as an activated sludge process

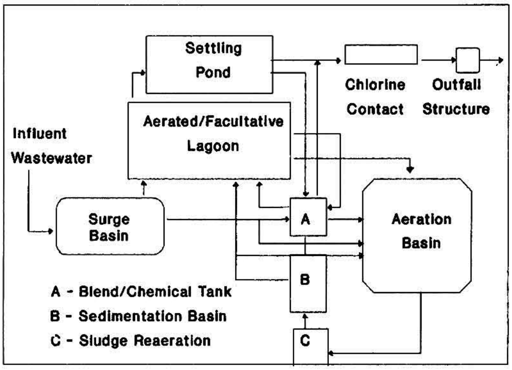

Figure 3. Modified process flow schematic.

were utilized to test its operational efficiency in various treatment modes including conventional first– and second–stage activated sludge, low and high–rate activated sludge, extended aeration, modified contact stabilization, modified Kraus process, and tertiary treatment process.

The historical and primary operating strategy for the Lagoon used most during the study can be described as a classical aerated/facultative lagoon. The 31,800 m^3 (8.4 MG) pond was operated as a continuous flow–through suspended-growth reactor with intermittent periods of solids recycle. It provided second–stage treatment as an aerated system, functioning in an aerobic, facultative, or anaerobic mode depending on organic loading. The Lagoon biochemically reduced and digested sludge from the first–stage sedimentation basin waste flows. It was also operated as a first–stage suspended–growth biological treatment system for waste stabilization of excessive organic loads or toxic pollutants diverted from entering the conventional activated sludge Aeration Basin system. Dissolved oxygen was supplied from 63 static tube aerators to keep the contents of the Lagoon in suspension and minimize odors which developed during periods of heavy organic loading. The diffused air system was operated continuously and output levels varied to maintain an aerated suspended–growth biological treatment system. Air flow to the first three rows of static tube aerators were intermittently reduced to establish an anoxic/oxic or anaerobic/aerobic process for removal evaluation of particular pollutants.

Parameter Collection and Sample Analysis

Analyses performed daily on the Aerated Lagoon during normal operating conditions are listed in Table 1. All analytical testing was performed in accordance with "Standard Methods for the Examination of Water and Wastewater" [*10*] COD was determined by the dichromate reflux titrimetic methods (Method 508B). BOD was determined using the standard 5-day testing procedure (Method 507). Biological solids (dissolved, suspended, and volatile) were determined through gravimetric methods at 108°C, 103°C, and 550°C respectively (Methods 209B-D). Total ammonia–nitrogen (NH_3-N), nitrate–nitrogen (NO_3-N), and orthophosphate (PO_4-P) concentrations were measured through colorimetric analysis. Sulfides (H_2S-S) were analyzed using the iodometric method (Method 427D). A digital pH meter with combination electrode was used to analyze the pH of all samples (Method 423). Dissolved oxygen was measured using an on–line dissolved oxygen analyzer with a zullig sensor probe. Sludge settleability was determined by the use of settleometers measuring 30-minute zone settling rates (Method 13D) and centrifuge spin sludge compaction tests [*11*]. Microbiological examinations of all sludge cultures were aided by the use of a phase–contrast electron microscope with 100X, 400X, and 1000X objectives.

TABLE 1. PARAMETER COLLECTION AND SAMPLE ANALYSES

Parameter	Influent	Reactor	Effluent
Flow	X		
% Sugar	X		
COD, BOD, SBOD	X	X	X
TSS, TDS, MLVSS	X	X	X
pH, alkalinity	X	X	X
Temperature		X	
DO, OUR, SOUR		X	
Settl, SSC, SVI		X	
NH_3-N, NO_3-N	X	X	X
H_2S-S, PO_4-P	X	X	X
Microorganisms	X	X	X
Color, odor, toxicity	X	X	X

BENCH–SCALE PILOT–PLANT EXPERIMENTAL APPROACH

Laboratory Apparatus

The bench–scale on–site pilot–plant (Figure 4) consisted of a plexiglass bio–oxidation unit [*12*]. The biological laboratory reactor unit contained an 8.5 L "complete–mixed, aerated lagoon basin" (mixed–liquor volume) and a 2.0 L "settling basin" (clarifier volume). The aeration basin and settling basin was separated by an adjustable, removable plexiglass baffle. The settling basin was equipped with an adjustable overflow weir, side slope of 4:1 to concentrate solids, and drainage line used as a sludge return or waste stream.

The air and feed supply to the laboratory unit was controlled with the use of a bio–oxidation console [*12*]. The console contained a variable speed gear motor to drive the input and output peristaltic liquid flow pumps, and a fixed speed gear to drive the solids removal pump. An average influent flow rate of 2.0 L/day produced a hydraulic retention time of approximately 102 hours (4.25 days) in the basins. Solids were removed intermittently from the clarifier at a fixed rate of 100 ml/hr via the control panel. An air supply switch on the console panel contained an air pump/flowmeter combination which provided an adjustable source of air, to a maximum of 15 ft^3/hr. The calibrated flowmeter/rotameter accurately measured air supply to ensure consistent test environments. An air diffuser stone and circular perforated tubing diffused oxygen into the bioreactor, to ensure complete mixing and desired dissolved oxygen levels.

Experimental Design

The pilot–plant provided independent control of process variables, enabling design, operating, and performance data to be evaluated for the specific sludge culture studied. The high strength industrial wastewater from the corn wet–milling and HFCS refinery processes was used as the feed stock and the active microbial biomass from the Aerated Lagoon was used as the sludge culture. Activated sludge for seeding the reactor had been acclimated to the high strength feed stock, so system start–up was minimal.

Fifteen operational runs were performed to determine the kinetics of biological growth for the Aerated/Facultative Lagoon treatment system. Mean cell residence time ($MCRT_c$) served as the primary control parameter.

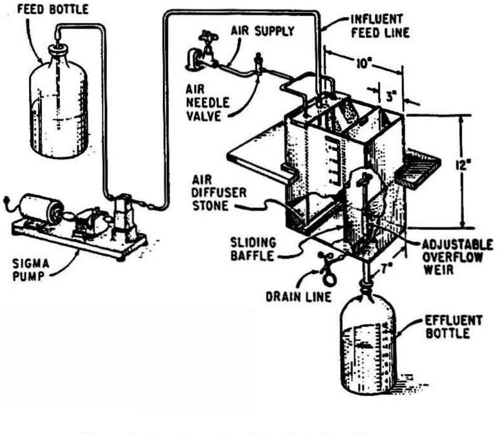

Figure 4. Bench–scale pilot-plant flow diagram.

Air flow rates were also adjusted to simulate dissolved oxygen levels which occurred in the full–scale operating Lagoon System. MCRTs were also operated at typical values for the Lagoon and maintained relatively constant by wasting and returning concentrated biological solids from the clarifier to the Aerated Lagoon Basin. Wasting of mixed–liquor suspended solids (MLSS) was performed intermittently at the end of each operating period, maintaining desired concentrations in the reactor and allowing the reactor to stabilize before sampling.

Steady–state conditions were assumed to exist when all operating parameters remained constant over a 48–hour period (~0.04 $MCRT_c$). Each test run was operated for at least 0.10 $MCRT_c$ value (~5 days) before problems with sludge settleability and solids washout occurred, requiring drastic changes in normal operation to regain process control. Composite samples of the pilot–plant feed, mixed–liquor, sludge underflow, and clarified effluent streams were collected in calibrated tanks for laboratory analysis: COD, BOD, DO, pH, temperature, MLVSS, SVI, TSS, nutrients (NH_3, NO_3, PO_4, and H_2S), and microbiological examination. Routine analyses were performed at steady–state conditions according to Standard Methods [*10*] and all other procedures previously described.

RESULTS AND DISCUSSION

Process Performance Summary

The overall performance and study results of the Aerated/Facultative Lagoon treatment system are summarized in Tables 2 to 5. These tables list the important parameters and analytical results obtained by the research. Original design values and operating parameters established for the Aerated/Facultative Lagoon are presented and compared with actual average values determined for the twelve months studied. Although numerous site specific results, analyses, conclusions, and recommendations could be made as a result of this study, several categorical subjects will be discussed, thus accomplishing the objectives defined for this paper.

The influent characteristics of the Coors BioTech raw wastewater, summarized in Table 2, show the high strength, soluble nature of corn wet-milling and syrup refining process wastes. The average organic strength of 4.4 kg/m³ (18.5 tons BOD/MG) is significantly higher than typical domestic sewage wastewater strengths of 0.2 kg/m³ (0-8 tons BOD/MG). The Coors BioTech carbohydrate–based wastewater was determined as being highly soluble in nature with a SBOD/BOD ratio of 0.755, suggesting a high level of biodegradability and biological treatability given enough process detention time.

Table 3 lists the operational parameters for the full-scale biological reactor. Summarized are research results which described the buffering capacity, oxygen transfer, solids inventory, sludge settleability, and nutrient concentration characteristics of the Aerated/Facultative Lagoon.

Summarized in Table 4 are effluent quality and discharge characteristics achieved by the Aerated/Facultative Lagoon process for high strength industrial waste stabilization.

TABLE 2. WASTEWATER INFLUENT CHARACTERISTICS

Parameter	Basis	Design	Actual
Flow	m³/month	23,470	13,280
	(MG/month)	(6.20)	(3.50)
Flow Split	percent (%)	00.0	45.0
Hydraulic Loading	m³/d	760	435
	(mgd)	(0.200)	(0.115)
Sugar Content	percent (%)	0-20	0.55
Feed Strength	mg/L COD	6700	5225
	mg/L BOD	4500	4350
	mg/L TSS	1500	1540
	mg/L TDS	13,200	13,210
	mg/L NH_3	30-200	280
	mg/L PO_4	40-160	70
	mg/L H_2S	10-100	90
Organic Loading	kg/m³	2.7	4.4
	(tons BOD/MG)	(11.4)	(18.5)
	kg/d	1030	1870
	(lbs BOD/day)	2270	4120
Organic Solubility	SBOD/BOD	0.70	0.755

TABLE 3. BIOLOGICAL REACTOR CHARACTERISTICS

Parameter	Basis	Design	Actual
Temperature	°C	20	19
pH	s.u.	6.5-8.0	7.8
Buffer Capacity	mg/L TDS		1500
Alkalinity	mg/L $CaCO_3$		690
Dissolved Oxygen	mg/L	0.0-4.5	1.9
O_2 Transfer Eff.	percent (%)	7-10	8.0
O_2 Suppl/BOD Rem	kg/kg	1.00	0.87
Solids	mg/L MLVSS	1000-4000	1800
Load (F/M)	BOD/MLVSS		0.03
MCRT	days		58
Settleability	ml/g SVI	<150	519
Nutrients	mg/L NH_3		62
	mg/L NO_3		14
	mg/L PO_4		64
Sulfides	mg/L H_2S		88

TABLE 4. WASTEWATER EFFLUENT CHARACTERISTICS

Parameter	Basis	Design	Actual
Carbonaceous	mg/L BOD	450	95
	mg/L TSS	150	61
Nitrification	mg/L NH_3		32
Denitrification	mg/L NO_3		9
Tertiary	mg/L PO_4		35
	mg/L H_2S		10

Organic Reduction

The Aerated Lagoon maintained a continuous mode of readiness to assimilate varying loads of high strength organic wastes. A wide range of organic loadings, 0-17.3 kg/m³ (0-72 tons BOD/MG), were tested and the Aerated/Facultative Lagoon demonstrated an ability to efficiently stabilize and treat the varying loads of BOD (Figure 5). The Lagoon exhibited an attractively high average BOD reduction (98.1%) for all loading rates, and performance increased when loadings were increased. Strict aerobic, facultative, and anaerobic modes of operation were utilized to evaluate BOD reduction efficiency.

The Lagoon's efficiency was highest (99.1%) when anaerobic conditions existed and slightly less (96.2%) under aerobic conditions. During conditions of low waste discharge and limited substrate available in the Surge Basin, the Lagoon was operated in continuous low-rate, intermittent, or non-feeding conditions. Lower removal efficiencies were observed at BOD loadings below 2.9 kg/m³ (12 tons BOD/MG), but without process upset. Peak performance was established at a continuous daily loading rate of approximately 4.4 kg/m³ (18.5 tons BOD/MG or 4100 lbs BOD/day). As organic loadings were increased, the process reached an optimum level of

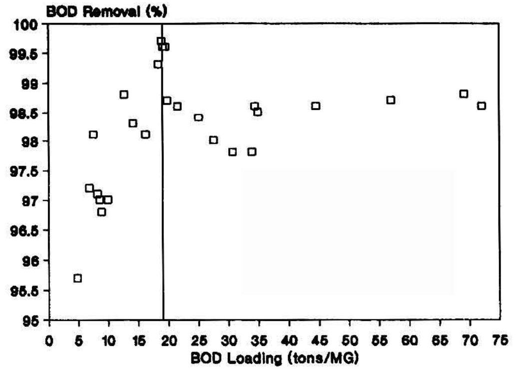

Figure 5. Organic (BOD) reduction results.

removal as seen in the plateau for removal rates above 8.4 kg/m^3 (35 tons BOD/MG). High performance in BOD reduction was a result of large reactor volume, adequate dissolved oxygen, sufficient nutrients, long MCRT, and a healthy–recalcitrant microbial biomass.

Process/Stream Flexibility

Process and stream flexibility of the Aerated/Facultative Lagoon was realized as the focal point in the Coors BioTech waste treatment process. The Lagoon operated efficiently in numerous treatment modes and was managed in such a way as to yield maximum benefit of treatment capacity for removal of numerous pollutants. In addition to the conventional first– or second–stage activated sludge treatment modes historically and most often used at Coors BioTech, other innovative uses of the Aerated Lagoon were essential at various times to maintain overall waste treatment process control. The Lagoon was operated in low– and high–rate activated sludge, extended aeration, modified contact stabilization, modified Kraus process, and tertiary treatment (anoxic/oxic and anaerobic/aerobic) modes. Table 5 lists the various treatment modes tested and expresses the performance results in terms of percent removal rates of each pollutant. Figure 6 illustrates the organic (BOD) removal efficiencies achieved by the Lagoon for each activated sludge process operated and tested during the research study.

A cursory review of the differences between the process flow schematics of the original WWTP (Figure 2) and the modified WWTP (Figure 3) illustrates the diverse process and stream flexibility of the Aerated/Facultative Lagoon. The study and testing of the process was not limited to strictly aerobic, facultative, and anaerobic modes of operation as a single–stage or second–stage system. Rather, innovative use and management of the system as a separate–stage or coupled process allowed for improvement and optimization of the overall Coors BioTech waste treatment plant.

TABLE 5. WASTEWATER POLLUTANT REMOVAL RATE EFFICIENCIES

Treatment Mode	Basis	Value
Overall	% BOD	98.1
	% TSS	91.4
Aerobic	% BOD	96.2
Facultative	% BOD	97.1
Anaerobic	% BOD	99.1
Low-Rate Activated Sludge	% BOD	97.0
High-Rate Activated Sludge	% BOD	98.7
Extended Aeration	% BOD	97.0
	% NH_3	89.6
	% NO_3	77.1
Contact Stabilization	% BOD	96.0
Tertiary	% PO_4	50.2
	% H_2S	88.9

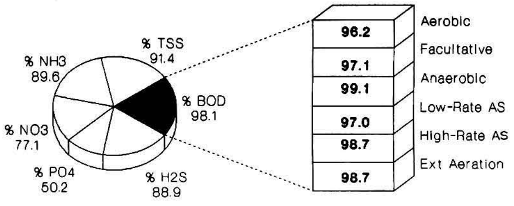

Figure 6. Organic (BOD) removal efficiencies.

Extended Aeration: During operating conditions as a low–rate activated sludge system, the air supply was systematically increased to provide advanced secondary treatment of biological removal of ammonia (NH_3-N) through nitrification. Sufficient microbial biomass concentrations (MLVSS) and high mean cell residence times (MCRT) allowed for easy process adjustments of increased dissolved oxygen (DO) levels to operate in an extended aeration treatment mode and achieve almost complete nitrification. Ammonia removal rates were observed to be 40% lower during winter time operation when the average mixed–liquor temperatures dropped 10°C in the Lagoon.

Anoxic/Oxic: A mixed–liquor recycle (MLR) stream was pumped from the tail end of the Lagoon to the head end using a submersible pump and conduit. The MLR stream served as single–stage nitrification/denitrification system operating in an anoxic/oxic (A/O) treatment mode. Tertiary treatment of nitrate (NO_3-N) removal was accomplished in the anoxic portion by turning down the air supply to the first three rows of static tube aerators. Air supply was maintained at a level necessary for maintaining solids in suspension but not sufficient to measure a residual dissolved oxygen concentration. The influent supply of BOD to the anoxic zone always exceeded the supply of available chemically combined oxygen in the nitrate. This ensured a driving force for oxygen uptake and oxidation of a portion of the soluble BOD by the facultative bacteria in the Lagoon's activated sludge. Simple process adjustments and stream flexibility allowed for successful nitrification and denitrification as an A/O process.

Anaerobic/Aerobic: During periods of cooling water and process water blowdown, the waste treatment plant experienced intermittent conditions of high phosphorus loadings. The Aerated Lagoon was operated in an Anaerobic/Aerobic mode similar to the previously described (A/O) flow configuration using the MLR stream. The difference in the MLR stream was the elimination of nitrates as an oxygen source. An accelerated uptake of phosphorus was identified using this biological removal process beyond the normal microbial growth requirements. The MLR stream stimulated the microorganisms to release the phosphorus in the anaerobic zone in the presence of BOD and then uptake and store the phosphorus in the biological solids of the aerobic zone as an energy reservoir for oxidation of BOD. The concentrated amount of phosphorus incorporated in the biomass was then removed by sludge wasting. This "luxury uptake" of phosphorus was observed to occur only during periods of non–nitrification as an Anaerobic/Aerobic process. Biological phosphorus removal did not appear to exceed the amount required for cell growth during process conditions of Anoxic/Oxic, as a coupled process with nitrification. It was determined that phosphorus and ammonia removal did not work well together in the Aerated Lagoon.

Modified Contact Stabilization: The recycle of sludge from the Aerated/Facultative Lagoon to the Aeration Basin system was instrumental in improving operating performance of the first–stage system during periods of process/plant upset. Lagoon sludge served as a viable seed sludge to develop a healthy microbial biomass and restore waste stabilization after intermittent periods of severe toxicity in the Aeration Basin system. During periods of high organic loading to the Aeration Basin, the proliferation of dispersed bacterial growth would cause poor sludge settleability and deteriorated effluent quality (high suspended solids). Recycling of Lagoon sludge characterized as stable settling sludge and comprised of numerous types of filamentous organisms, provided the microstructure needed for proper bacteria floc formation. Proper floc formation improved the sludge settleability and biological solids removal in the Aeration Basin system. The Lagoon also served as the source of trace metals, nutrients, and alkalinity to the Aeration Basin system by returning supernatant from the Settling Pond to the Chemical/Nutrient Blend Tank. This return stream was frequently used to control the food–to–microorganism ratio (F/M) in the Aeration Basin and sustain a proper relationship between organics and biomass for stable operation.

Modified Kraus Process: The return of anaerobically digested Lagoon sludge and supernatant from the Settling Pond to the Chemical/Nutrient Blend Tank also functioned as a modified Kraus process. The supernatant was rich in ammonia, nitrate, and alkalinity. It was blended with RAS from the first–stage sedimentation basin to correct nitrogen deficiencies in the high–carbohydrate waste. The heavy solids of the digested sludge improved the settleability of the Aeration Basin mixed–liquor.

Biological Solids Removal

A simulated clarification evaluation through the use of a settleometer showed an average high suspended solids removal rate (96.5%). The Al West Method [*11*] was used to evaluate sludge settling characteristics. Zone settling rates using 1000 ml settleometers and percent sludge settled concentrations (SSC) using centrifuge spin tests were correlated between the Aeration Basin/clarifier system and the Aerated/Facultative Lagoon system to allow solids removal for the Lagoon to be evaluated. It is recognized that installation of a sedimentation basin on the outflow of the Lagoon would effect most accurate results of process suspended solids removal and clarification, but such facilities did not exist. Although the second–stage Settling Pond acted as a clarification pond of Lagoon mixed–liquor outflow, most research data between Lagoon laboratory settled effluent and Settling Pond supernatant did not correlate well.

Biological solids removal efficiencies were observed to decrease at low and high organic loadings (Figure 7) and lower MCRTs. As will be discussed in the next section, the deteriorated effluent quality for suspended solids was strictly a function of sludge settleability and organic loading. The highest suspended solids removal rates were observed to occur at an average organic loading rate of 4.4 kg/m^3 (18.5 tons BOD/MG). Maximum treatment performance in BOD and suspended solids removal were achieved during average loading conditions of 3.6-6.0 kg/m^3 (15-25 tons BOD/MG). Simultaneous microscopic examinations showed a well–balanced population of filamentous organisms in the activated sludge. The filaments provided the necessary microstructure for the bacteria to flocculate and settle nicely in the clarification process. They also served to efficiently filter and capture dispersed bacteria, thus decreasing the concentration of suspended solids in the clarified effluent.

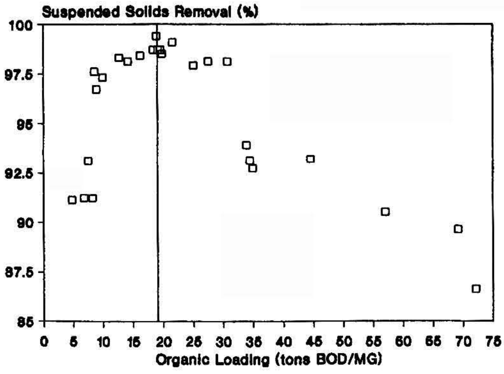

Figure 7. Suspended solids removal results.

Sludge Settleability

Despite Lagoon sludge settleability rates (average SVI = 520 ml/g) characteristic of bulking sludge conditions (defined as SVI > 150 ml/g) [*13*], excellent solids compaction and filterability properties were observed. Settleometer tests (30–minute) showed a slow settling rate with a constant, uniform, well defined sludge blanket, good sludge compaction, and clean clarified supernatant. Biological solids in the Lagoon demonstrated predictable settling characteristics for all months studied. Its settleability rates were sensitive to sharp changes in BOD loading. Settling deteriorated if the organic loading occurred outside the normal operating envelope of 3.6-6.0 kg/m^3 (15-25 tons BOD/MG). As observed in Figure 8, the peak performance in sludge settling, expressed as settled sludge concentration (SSC) occurred at 4.4 kg/m^3 (18.5 tons BOD/MG).

A persistent–bulking condition was observed during very high organic loadings. Sludge settleability improved as BOD loadings approached average loading conditions. High organic loading rates caused the formation of polysaccharides or viscous bacterial slime and poor settleability. This slime or jelly formation of extracellular mass was highly water retentive. Initially termed "viscous bulking," it has been more recently recognized as "zoogleal or non–filamentous bulking" [*13*]. The Lagoon's settleability behaviour suggested classical "bulking

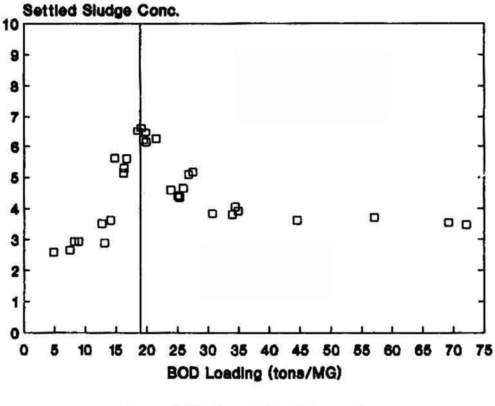

Figure 8. Sludge settleability results.

sludge." However, high SVI or low SSC values were not the result of abundant or excessive filamentous organism growth which extended into bulk solution and formed bridges between the floc, causing poor settleability and compaction. Daily microscopic examinations of the Lagoon's activated sludge identified numerous types of filaments, at a constant count in the common range (1-5 filaments/bacterial floc) to very common range (5-20 filaments/floc). This level of filaments coupled with rapid changes in BOD loading and intermittent presence of polysaccharides caused a consistently slow settling of biological solids.

Microbiology

General microbiological characteristics were examined and showed a stable, healthy, recalcitrant microbial biomass comprised of a well–balanced population of bacteria, fungi, "bugs" (protozoa and rotifers), and filaments. The Aerated Lagoon maintained sufficient and excess levels of important nutrients (C, N, O, P and S) and trace metals to enhance and sustain healthy microbial life and growth. Average nutrient concentrations present in the mixed–liquor were: $O_2 = 2$ mg/L, NH_3-N = 62 mg/L, NO_3-N = 14 mg/L, PO_4-P = 64 mg/L and H_2S-S = 10 mg/L. Levels of monthly nutrients showed no conclusive trends or changes when the Aerated/Facultative Lagoon system was not operating in a tertiary treatment mode to provide stabilization and removal of particular pollutants.

Elevated levels of ammonia and sulfides were present when known concentrated discharges of these chemicals were diverted to the Lagoon for treatment. Influent concentrations of ammonia as high as 1000 mg/L were successfully treated by operating the Lagoon in an advanced secondary mode and biologically removing the ammonia through nitrification. During periods of high ammonia loading, an average concentration of 312 mg/L was nitrified to a level of 32 mg/L. The demonstrated removal rate efficiency was 89.6%. Nitrates formed by the nitrification process were simultaneously reduced 77.1% through denitrification, to a concentration of 9 mg/L using the anoxic/oxic process. Agricultural ditch water used for cooling water in the wet–milling and syrup refining process was intermittently discharged to the wastewater treatment plant at an average influent concentration of 71 mg/L. The anaerobic/aerobic process coupled with sludge wasting removed an average of 50.2% of the influent phosphorus load. High loadings of sulfide in excess of 100 mg/L were utilized by the bacteria, as evidenced by microscopic observations of large black areas of elemental sulfur in the mixed–liquor, which had precipitated from oxidation of hydrogen sulfide. This uptake of sulfides into the bacterial floc reduced the influent concentration by 88.9%, to an average effluent value of 10 mg/L.

Toxicity

The Aerated Lagoon's microbial biomass was resistive to toxicity from acute loadings of highly concentrated wastes of ammonia, sulfides, acids, caustic, and biocides. Dissolved oxygen (DO) uptake testing, endogenous respiration rate monitoring, and specific oxygen uptake rate (SOUR) analyses demonstrated the Lagoon's unique ability to resist and remain unaffected by toxic material at high concentrations in the Surge Basin.

Due to the use of sulfur dioxide in the wet–milling process for "cracking the corn," and use of ammonia in refining the HFCS, the waste treatment plant was regularly loaded with extremely high, potentially toxic levels of sulfur and ammonia. The raw waste stream was observed to contain concentrations of hydrogen sulfide in excess of 100 mg/L and ammonia greater than 1000 mg/L. Discharge of these toxic materials in sufficient quantities were suspected to have caused plant upsets and toxicity (complete inhibition of bioactivity) to the Aeration Basin activated sludge system. Toxicity resulted in lower BOD and TSS removal rates, dispersed and deflocculated bacteria, decreased bacterial growth and waste stabilization activity, foaming, and sludge bulking.

Evaluation of the toxicity potential to both biological systems was accomplished by a wastewater treatment plant detection and control of toxicity endangerment assessment study, performed during the research period. The study focused on the oxygen uptake rate (OUR) as a measure of the relative rate of aerobic metabolism, activity, and viability of the microorganisms. The test, when related to other process parameters, indicated specific levels of bioactivity (SOUR), trends, and metabolism rates as a result of suspected toxic chemical agents, low or high pH wastes, and nutrient deficient levels in the biological reactors.

As seen in Figure 9, testing on January 5, 1987 of suspected toxic material present in the Surge Basin, shows significant differences between Aeration Basin and Aeration Lagoon microbial activity and sensitivity to toxicity. The acidic waste tested (pH = 1.8 and NH_3-N = 180 mg/L) when introduced to the Aeration Basin resulted in a sharp drop in OUR, where this same material had no adverse effects on the Lagoon sludge culture. The Aeration Basin SOUR profile indicates a clear sign of toxicity, where the waste in concentrations greater than 1% by volume, caused a rapid depression of the OUR of the sludge culture. The value of SOUR on the ordinate (Aeration Basin = 21 mg O_2/g-hr and Aeration Lagoon = 16 mg O_2/g-hr), corresponds to the endogenous respiration rate of the bugs where no waste was introduced and organic substrate was limiting. The profile shows that wastes in

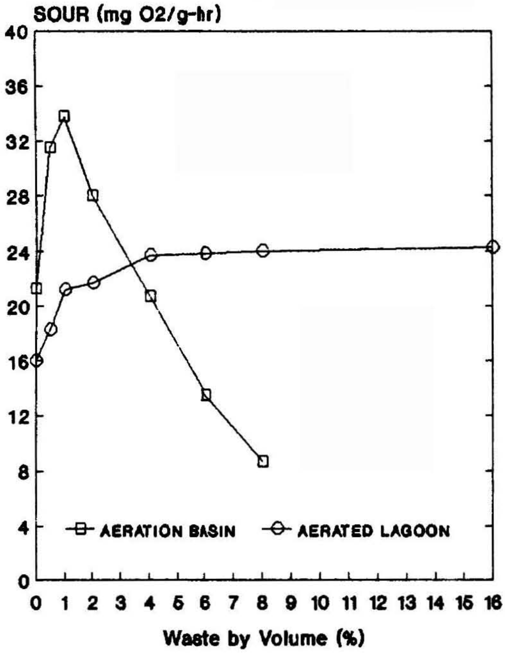

Figure 9. Toxicity assessment for acidic waste collected 1-5-87.

concentrations greater than 4% by volume, reduced the SOUR below the basal or level of natural endogenous respiration. Values below this base level will result in cell lysis and death.

Figure 9 also shows the specific OUR profile for the Lagoon, where the waste tested showed nontoxic effects. An optimum level of oxygen uptake was achieved and maintained. Further analysis through several months of testing of various suspected toxic wastes (low pH < 3.0, high pH > 11.0, ammonia > 300 mg/L, and sulfides > 100 mg/L), showed conclusively that the Aerated/Facultative Lagoon sludge culture was quite resistive to toxicity. In no case could enough volume of a particular harmful toxic waste or chemical agent be introduced into the system to adversely impact the microbial biomass and performance levels of the Lagoon (Figures 9 and 10).

Since toxicity or death of the microorganisms did not occur in the Lagoon, it was successfully used to mitigate process upsets and potential toxicity to the more sensitive first-stage Aeration Basin system. Problematic wastewater and shock loads of BOD or chemicals present in the Surge Basin were automatically diverted to the Lagoon for stabilization and treatment. Table 5 lists the removal confidence rates for BOD, TSS, ammonia, nitrate, phosphorus, and sulfides observed during known concentrated discharges. Large reactor volume, sufficient aeration, long detention time, high alkalinity and buffering capacity, and a very stable, healthy–recalcitrant microbial biomass were attributed to the Lagoon's unique ability to absorb, stabilize, and treat problematic and potentially toxic industrial wastes.

Pilot–Plant Steady–State Data Summary

A summary of the steady–state data obtained from the pilot–plant is presented in Table 6. An average 95.5% BOD reduction and 80.1% suspended solids removal were observed over the duration of the six–month pilot-plant study. The bench-scale reactor's efficiency in BOD reduction was distinctly more consistent with the full–scale Lagoon reactor than suspended solids removal. Characteristic high strength feed wastewaters resulted in average effluent BOD concentrations representative of the actual performance of the Aerated Lagoon system. Table 6 also provides steady–state summary data of actual performance of the full–scale Aerated Lagoon treatment system during the same months of the pilot–plant study. Twenty–three test runs were conducted from December 1986 to May 1987. These performance data were used to verify the effluent results from the pilot–plant, as well as the biological kinetic coefficients determined from the model. Identical system parameters were measured and evaluated for the bench– and full–scale plant data, to establish calibration and model verification. High BOD reduction efficiencies in the bench–scale reactor were a result of sufficient MCRTs and a healthy, viable Lagoon sludge culture acclimated to highly soluble organic waste.

Operational problems with the pilot–plant became evident in the erratic and unpredictable effluent suspended solids concentrations. The Lagoon's performance in TSS removal can not be derived from pilot–plant performance. An average 16% lower TSS removal efficiency was observed experimentally between pilot–plant and actual plant data. This discrepancy is explained by insufficient hydraulic retention times in the bench–scale settling basin, which prohibited proper settling of a characteristically slow settling sludge. Problems with maintaining steady–state reactor MLSS concentrations led to solids washout, rapid growth of filaments, sludge bulking, foaming, and eventual loss of process control. Poor settling characteristics and sludge compactibility resulted in solids carry over the settling basin effluent weir and thus lower suspended solids removal efficiencies.

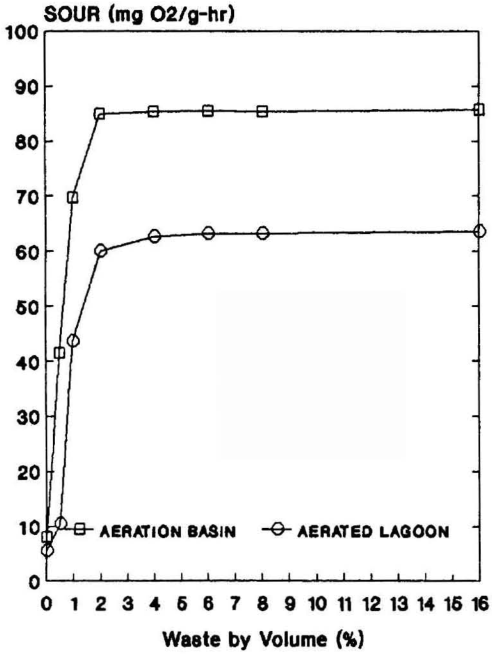

Figure 10. Toxicity assessment for industrial waste collected 3-14-87.

Biological Growth and Kinetic Coefficients

Although not presented in this paper, the pilot–plant study did provide a large amount of useful information about the biological suspended–growth kinetics of the Aerated/Facultative Lagoon [6]. Examination of the microbial growth rates and biokinetic coefficients showed that the high strength wastewater and specific biological growth rates for the Aerated Lagoon's microbial biomass, in its industrial waste treatment setting, did not allow for a first–order, steady–state kinetic model which is used primarily to model low strength sewage treatment systems, to be adequately and effectively applied. Rather, the Lagoon's industrial waste treatment application, specific environment and growth rates, operational characteristics, and resulting levels of performance would be more appropriately applied to a dynamic, higher–order removal rate model which is capable of mathematically describing the complex physical, chemical, and biological processes occurring within lagoons.

TABLE 6. PILOT-PLANT AND LAGOON SUMMARY STEADY–STATE DATA

Parameter	Basis	Pilot–Plant	Aerated Lagoon
Influent	mg/L BOD	5500	5475
Solids	mg/L MLVSS	1660	1590
MCRT	days	51	58
Effluent	mg/L BOD	139	95
	mg/L TSS	327	61
Removal Rates	% BOD	95.5	98.1
	% TSS	80.1	96.5

SUMMARY AND CONCLUSIONS

The performance and kinetics of an Aerated/Facultative Lagoon suspended–growth biological treatment system were examined for high strength industrial waste stabilization. A pilot–plant study provided a large and useful database of information about the biological growth kinetics and expected levels of performance of the Coors BioTech Aerated Lagoon for various organic loadings and environmental conditions. This breadth of experimental knowledge coupled with the results of the overall study were used to develop an innovative management program for the Lagoon treatment system. The Lagoon was operated in various treatment modes and over a range of organic loadings and influent wastes to demonstrate its performance capabilities for high strength industrial waste stabilization.

It follows that aerated/facultative lagoons used in industrial waste treatment applications contain specific environments, growth rates, influent and operational characteristics, and resulting levels of treatment performance. Developing an innovative lagoon treatment program, which effectively manages the system and utilizes its capabilities, can improve and optimize overall performance in waste stabilization at an industrial treatment facility. The Coors BioTech Aerated/Facultative Lagoon treatment system is just one example.

From the investigation results, the following conclusions were formed:

- The innovative management and use of the Aerated/Facultative Lagoon is essential in the waste treatment process at Coors BioTech.
- Process stream flexibility, large reactor volume, adequate aeration, sufficient nutrients, long mean cell residence time, high buffering capacity, and healthy–recalcitrant microbial biomass significantly contribute to its excellent efficiency in high strength industrial waste stabilization.
- Aerated/facultative lagoons can provide effective treatment in various operational modes.
- High strength soluble industrial waste stabilization using aerated/facultative lagoons are more appropriately described by a dynamic, high–order removal rate mathematical model.
- Research results presented of the performance and kinetics of the aerated/facultative lagoon suspended–growth biological treatment system suggest and confirm the importance and applications of such treatment processes as a viable alternative for high strength industrial waste stabilization.

ACKNOWLEDGMENTS

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Removal of Organics from Offshore Produced Waters Using Nanofiltration Membrane Technology

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The separation of oil and produced water mixtures from oil and gas producing wells has traditionally been accomplished by gravity settlers (e.g., multi-phase separators, skimmers, and flotation cells). However, current EPA regulations on the organic content of discharged produced water have reached the limits of these separation techniques. The industry is in need of new technologies to treat these waters. One such technology that we have found promising is organics/water separation by nanofiltration membranes.

INTRODUCTION

On offshore production platforms, high-salinity produced water can be discharged overboard after removing as much of its residual oil as required. The monthly average organics limit of discharged offshore produced water is 48 mg/L, as measured by EPA Method 413.1. At this level, the majority of these organics are often soluble, and therefore not removable by phase separators such as skimmers and flotation cells. Reinjection is often not an alternative, and activated carbon adsorption can be expensive and troublesome on a large scale offshore. The industry is in need of new technologies to treat these waters. One such technology that we have found promising is organics/water separation by nanofiltration membranes. We are developing a treatment process for offshore produced water that employs nanofiltration and eliminates the need for gas flotation cells and large carbon scrubbers. We have built and are operating a pilot unit designed to test this process on offshore platforms.

PROCESS BACKGROUND

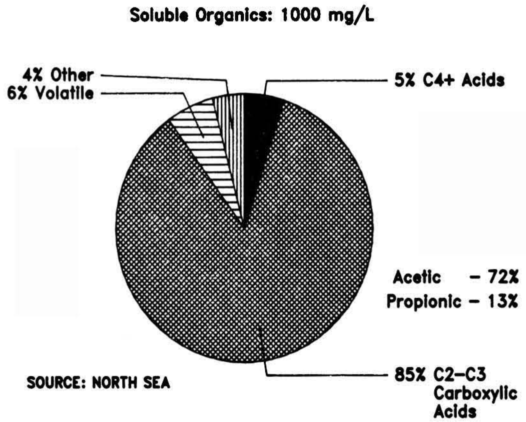
The rejected solutes in a membrane separation process increase in concentration as the water flows from the inlet (feed) to the outlet (reject) of a membrane unit, due to the passage of water at a significantly lower solute concentration (permeate) through the membrane. If the feed is concentrated only differentially on the brine (feed → reject) side of the membrane, the percent rejection of a particular solute by a membrane can be determined from:

$$\frac{(\text{feed concentration} - \text{permeate concentration}) \times 100}{\text{feed concentration}}$$

The absolute concentration of the solutes that are rejected can affect their rejection behavior. Therefore, this equation, when applied to a membrane separation system with a large recovery (% recovery = permeate rate × 100/feed rate), defines the % rejection at a particular brine concentration or membrane location between the inlet and outlet points of the unit.

Nanofiltration (NF) membranes are permeable to water and monovalent inorganic ions and relatively impermeable to many organics and divalent inorganic ions. Sodium chloride rejections are typically 0% to 20%. Organic acid rejections (80% to 100%) increase with molecular weight. NF membranes exhibit very high rejections of organics greater than 300 molecular weight. Divalent inorganic ions have rejections varying from 30% to 90% at produced water concentrations. By comparison, reverse osmosis (RO) membranes can show rejections of 95% to 100% with all these ions.

The major soluble organic compounds found in produced waters are low molecular weight carboxylic acids and volatile hydrocarbons. Figure 1 illustrates a typical distribution reported by Somerville, *et al.* [*1*]. Typically, 80%-90% of the soluble organics are C_2 and C_3 carboxylic acids. Higher molecular weight carboxylic acids up to C_{10}



SOURCE: NORTH SEA

Figure 1. Typical profile of soluble organic compounds in produced water.

are usually found at much lower concentrations. There can be a great variety of C_6 to C_8 organics in the "other" fraction.

We have shown in laboratory testing that the carboxylic acids in produced water are substantially rejected by NF membranes, with the rejection increasing at higher pH. The other low molecular weight organics found in produced waters (*e.g.*, volatiles, single-ring aromatics) more readily pass through these membranes. The higher molecular weight insoluble hydrocarbons typically suspended in produced waters are almost completely rejected.

The rate of water flow per unit area of membrane, or flux, is a function of temperature (flux increases with temperature), and the apparent transmembrane pressure drop: (brine pressure − permeate pressure − brine osmotic pressure + permeate osmotic pressure). The osmotic pressures are mainly dependent on the inorganic solute concentrations in each stream, and vary along the stream paths within a membrane unit, especially at high recoveries. Predicted fluxes with standard feed waters (similar to the waters that might be processed with the particular membrane) are usually reported by manufacturers at recoveries of 5%-10%.

Figure 2 shows a typical profile of inorganic ions in one of our own produced waters. Since NF membranes are relatively transparent to NaCl at produced water concentrations, NaCl exhibits little effect on the apparent transmembrane pressure drop, and these membranes achieve good fluxes with produced waters at much lower pressures than possible with RO membranes. Divalent inorganic ions are partially rejected to varying degrees and are usually present in produced waters at higher concentrations than the soluble organics, so their behavior effects the operation of an NF separation process significantly.

LABORATORY EXPERIMENTS

The current average monthly limit for discharge of offshore produced waters to the ocean is 48 mg/L total organics, as measured by EPA Method 413.1. This is a measure of the organics which are extracted out of 1 liter of produced water by 100 mL of fluorocarbon-113(1,1,2-trichloro-1,2,2-trifluoroethane), hereafter called freon. In this test, organics are measured gravimetrically after evaporation of the solvent. The test is typically run in onshore laboratories. Offshore, EPA Method 413.2 is used for self-monitoring purposes. The extraction method is the same as in 413.1, but a scanning (or non-scanning) IR spectrophotometer is used to determine the organic content in the freon phase by measuring the absorbance (relative to the baseline) of the peak maximum at 2930 cm^{-1} (C—H bond) and comparing this to standard absorbances. For produced waters, the value obtained by Method 413.1 (the gravimetric test) is slightly smaller than that obtained by 413.2 (the IR test), due to the loss of volatiles which occurs in the former by evaporation during the test and the extra handling involved. Since 413.2 is easier to do offshore, and arguably more accurate, we have used it as our standard test for analyzing produced waters and determining the behavior of the NF membranes, both offshore and in our laboratories.

To differentiate between what was probably a nonsoluble hydrocarbon in the produced water sample from what was probably a soluble non-hydrocarbon (*e.g.*, carboxylic acid), an additional measurement can be made after using silica gel to adsorb the polar (non-hydrocarbon) FEO from the freon solution (Standard Method 5520F, 17th Ed., Standard Methods for the Examination of Water and Wastewater). The remaining hydrocarbon fraction, or "free" oil, is measured, and non-hydrocarbon FEO inferred from the difference between the total and free oil measurements.

In our laboratories we used a Nicolet 5DXC FT-IR spectrometer for studying relative organic concentration differences over a broad IR spectrum, but the data included in this report are from the 2930 cm^{-1} peak measurement. We also determined the total organic carbon content of the tested waters directly with a Dohrmann Carbon Analyzer model CD90. Specific organic species were identified with a VG mass spectrometer, model 7070.

The inorganic cations were determined by a Jarrell-Ash Inductively Coupled Plasma Atomic Emission spectrometer, model 975. Chlorides were determined by silver nitrate titration, and carbonate and bicarbonate anions were determined by sulfuric acid titration. Overall inorganic rejections were estimated using a Yellow Springs Instruments model 32 conductance meter.

We made a study to determine which of the organic compounds that are soluble in produced water are also extractable with freon, and in general found that freon is *not* a good solvent for the major produced water organic species. Figure 3 illustrates our findings, using dilute (<1000 mg/L) C_2 to C_8 carboxylic acid solutions. A comparison of Figure 4 with Figure 1 shows a similar result with produced water. Only the C_4 and higher carboxylic acids and some of the other compounds found in the water studied extracted into the freon. This solvent/solute relationship was not significantly affected by the total ionic strength of the water tested. These results helped explain our finding that the total organics content of a produced water estimated using the TOC analysis result

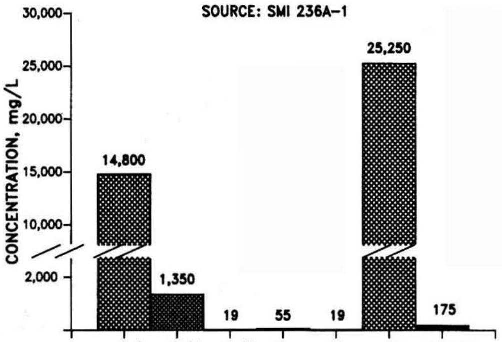


Figure 2. Typical profile of inorganic ions in produced water.

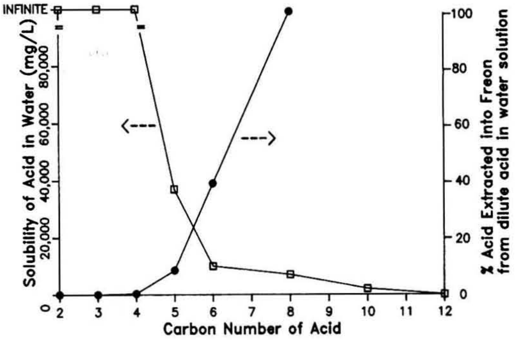


Figure 3. Solubilities of carboxylic acids in water compared to the ability to extract the acids from dilute acid-in-water solutions (<1000 mg/L) with fluorocarbon-113 (freon).

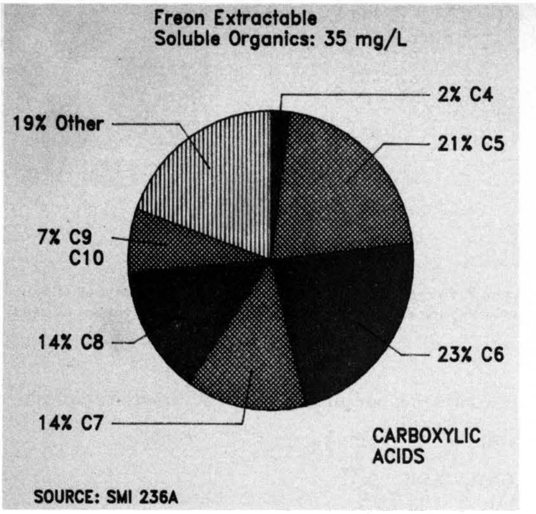


Figure 4. Typical profile of water-soluble organics which can be extracted by fluorocarbon-113 (freon) from produced water.

could be up to 20 times higher than the level determined by EPA 413.2.

It should be noted that most of what are *not* being picked up by the EPA tests are C_2 and C_3 carboxylic acids, which are rejected by NF membranes, although to a lesser extent than the higher acids. These lower molecular weight organic acids have also been shown to be readily biodegradable [*1*]. The EPA test, then, seems to give an adequate measurement of the least biodegradable organics in produced waters.

Since the EPA test methods selectively measured C_4 and higher carboxylic acids and not the lower molecular weight acids, and since NF membranes reject the former better than the latter, we decided to investigate using these membranes as part of a new treatment process for offshore produced waters. The relative amounts and types of organics and inorganic ions in each formation's produced water varies significantly, so the applicability of this NF treatment process must be determined separately for different platforms. Different manufacturer's membrane samples were fed samples of produced water from several of our gulf coast platforms. The membranes were held in 30 mm diameter stainless steel flow cells. The standard test conditions were a feed pressure of 14.8 bar (200 psig) at 30°C-40°C. Temperature and pH were varied and their effects on the membrane's performance evaluated.

We found a strong dependence of organic rejection on the pH of the produced waters. Some waters had low rejections at their original pH, but it was found that the rejections could be improved by adding caustic soda to increase pH. Other waters showed no improvement in organic rejection above their initial pH, but exhibited a drop-off in rejection at lower pH. We found this effect to be true with the tested produced waters and a simulated produced water composed of 250 mg/L hexanoic acid and 40,000 mg/L NaCl in deionized water. Typical relationships for FEO, TOC, and inorganic rejections versus pH are shown in Figures 5 and 6. As a class, the different membranes tested rejected the FEO in the produced waters studied well enough to meet the 48 mg/L criteria in the permeate.

Measured free FEO concentrations in the permeate were typically below 10 mg/L, and the uncertainty of the measurement offshore was found to be 3 mg/L. Since attempting to quantify free versus soluble rejections with this relatively large error resulted in a much larger, but fictitious, variation in calculated soluble rejections, we have reported only total FEO rejections.

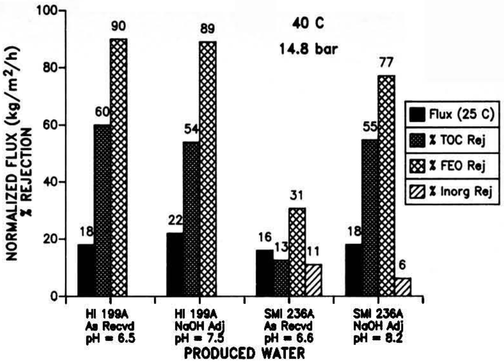


Figure 5. Performance of a typical nanofiltration membrane with two different produced waters before and after pH adjustment.

The necessity of increasing the pH to effect good rejections depended on the water being tested, not on the brand of membrane tested. Whether increasing the pH would be economically feasible to do offshore as part of a treatment process would depend on the value of the platform's product in relation to the amount of produced water that must be treated. Early in a well's production life, when the ratio of oil to water is usually high, it could be cost effective to adjust the produced water pH during treatment, whereas this may not be the case as the well becomes depleted and the relative produced water rate begins increasing.

The passage through the membrane of inorganic solutes with the water is highly desirable to lessen their buildup in the separation system. As solute concentration increases in the membrane separation system, the flux could decrease due to increased osmotic pressure and/or precipitation of a relatively insoluble salt at the membrane surface. We also recognize that raising the water's pH may exacerbate this potential problem. We are now beginning a laboratory program to study the effect of increased concentrations of solutes on % rejection, flux, and fouling in the NF system. We have redesigned our lab's bench-scale unit to be able to evaluate membranes in spiral-wound and tubular configurations. We are in the process of evaluating other brands of NF membranes, looking for those with the highest rejection of organics and lowest rejections of divalent inorganic ions.

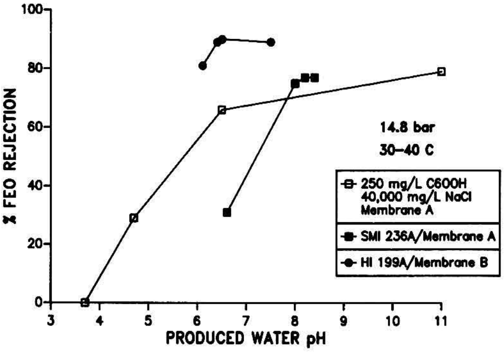


Figure 6. Effect of pH on % FEO rejection of nanofiltration membranes with two different produced waters and a hexanoic acid/NaCl brine.

PILOT PLANT STUDIES

The initial results from the laboratory tests were promising enough that it was decided to build a small pilot unit that could be easily transported to our offshore platforms. We designed a pilot unit based on the U.S.-manufactured standard 2.5 inch (6.35 cm) spiral-wound module. The typical flow rate through these modules is 9.5 L/min, or, in U.S. oil industry units, about 85 barrels per day (BPD). A heat exchanger is installed to cool produced waters with temperatures up to 65°C, down to below 45°C, a typical operating temperature limit for many NF membranes. Because of the explosion-proof requirement for platform equipment and the harsh operating environment found there, we kept the use of electronic process control equipment to a minimum. A pH controller in an air purged cabinet is the sole device of this type on the unit. Pressure and flow control is obtained with self-actuated automatic control valves, and the other control elements are simple air-operated switches typically used on offshore platforms. Battery-powered (less than 9V) indicators were used where available. We used CPVC instead of stainless steel wherever possible, and this has held up much better, both inside and out. A process flow diagram of the pilot unit is shown in Figure 7.

At this time, the pilot unit has been tested on various Texaco platforms. The total FEO rejections have ranged from 72% to 89%, mainly dependent on the membrane used. Overall inorganic rejections have been 15%-20%. Comparisons between offshore and onshore results with the same water shows slightly lower rejections offshore. We suspect that this is due to the volatiles measured in the water offshore which are, for the most part, lost during handling when tested onshore.

Productivity data have been obtained with a feedwater of 58,000 mg/L total dissolved solids (TDS). Preliminary results show that the different NF membranes we are testing have normalized (25°C) productivities ranging from .5 to 1.2 m^3/day (about 4% to 9% recovery) for a standard 6.35 cm diameter, one meter long spiral-wound module at 14.8 bar after two days onstream. Based on the reported membrane area of the modules tested, a flux of 11 to 18 kg/m^2/h was obtained. The effect of operating pressure on flux was linear between 11.2 and 18 bar. We are continuing our pilot unit tests at various Texaco producing facilities.

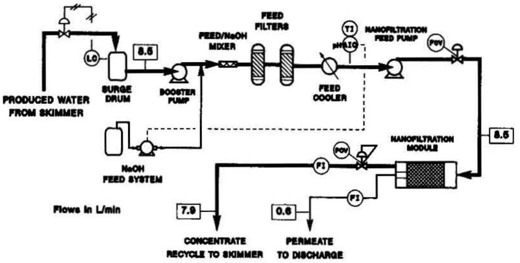


Figure 7. Process flow diagram of skid-mounted pilot unit used offshore for testing the ability of nanofiltration membranes to remove organics from produced waters.

CONCLUSIONS

We propose that nanofiltration membranes, as a class, when fed a produced water of up to 176 mg/L freon-extractable organics, will yield a permeate for discharge of less than 48 mg/L freon-extractable organics at 50% recovery, while rejecting less than 20% of the NaCl. This is based on an expected FEO rejection of 80%. For a standard 6.35 cm diameter by 1 meter long spiral-wound module, initial productivities at 25°C, 14.8 bar, 58,000 mg/L TDS, and 7% recovery can be expected to be as high as 1.2 m^3/day (7.5 BPD). Although more development work is needed for this application, NF membrane systems have the potential to replace flotation cells and/or carbon adsorbers on platforms where these are required.

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Design Considerations for Soil Cleanup by Soil Vapor Extraction

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The development and application of innovative technologies for soil remediation is rapidly evolving. Soil vapor extraction has been identified as one of the most attractive technologies for remediating volatile organic compounds in unsaturated zone (above the groundwater table) soil, because it is effective and economical. However, the design basis for applying this technology is not well documented. This paper presents a state-of-the-art approach for design and implementation of a soil vapor extraction system to remediate soil at a federal site in the Midwest contaminated with tetrachloroethylene.

INTRODUCTION

One of the most attractive technologies for remediating soils contaminated with volatile organic compounds (VOC) or light petroleum hydrocarbons, such as gasoline, is soil vapor extraction. Also known as soil venting or vacuum extraction, this method can usually be performed within a relatively short time and for minimal cost.

Typical remediation costs for soil vapor extraction at small sites with shallow soils in the unsaturated zone are approximately $30 to $60 per cubic yard (0.8 cubic meter). Typical remediation times are four to eight months. Actual remediation costs and times will vary from site to site and depend on many factors, such as contaminant type and quantity, areal extent and depth of soil contamination, and soil stratigraphy [*1*].

APPLICATIONS

Soil vapor extraction has proved to be effective for the removal of VOC and light petroleum hydrocarbons from subsurface soils beneath underground storage tanks and pipelines as well as in surficial spill areas. It can be applied either *in situ* to subsurface soils, or above ground to excavated soil piles. When applied *in situ*, very little above-ground space is required; hence, disruption to surface activities is minimal. In certain situations, soil vapor extraction can be combined with bioremediation to remediate unsaturated zone soils containing less volatile residual contaminants or it can be integrated with groundwater treatment systems for complete remediation of the unsaturated and saturated zones.

Soil vapor extraction is performed by applying a vacuum to the soils to induce volatilization of soil contaminants. The extracted air is usually treated for VOC removal prior to discharge to ambient air. However, treatment requirements depend on the air discharge regulations of the state in which the project is located. Currently available treatment technologies for the extracted air include activated carbon adsorption, incineration, and biofiltration.

Typical data requirements necessary for site characterization and soil vapor extraction system design are presented in Table 1. The amount of data and analyses needed for such characterization and design depends on the size and complexity of the site. For example, a small site with homogeneous and isotropic soil and a single contaminant will require less data and analyses than a

TABLE 1. DATA REQUIREMENTS FOR SITE CHARACTERIZATION AND SYSTEM DESIGN

Data Requirement	Method of Data Collection
Areal and Vertical Extent of Soil Contamination	Soil Borings, Soil Gas Survey
Areal and Vertical Extent of Groundwater Contamination	Groundwater Monitoring Wells
Depth to Groundwater	Groundwater Monitoring Wells
Physical Properties of the Soil	Lab Analysis, Borehole Geophysics
Contaminant Type and Concentration	Field and Lab Analyses
Chemical Properties of Contaminants	Reference Materials, Lab Analysis
Soil Cleanup Standards	Regulatory Agency and/or Risk Assessment

large complex site with heterogeneous and anisotropic soils containing multiple contaminants. Analytical tools such as computer models can be used for evaluating proposed designs of the soil vapor extraction system.

The data presented in Table 1 are required to evaluate the feasibility of applying soil vapor extraction at a specific site. In general, the contaminants must have sufficient volatility, and the soil must have sufficient air permeability for soil vapor extraction to be feasible. Sometimes a fraction of the site contaminants is sufficiently volatile to be removed by soil vapor extraction, and the remaining fraction is not. If the nonvolatile fraction is biodegradable and the soil has sufficient air permeability, it may be possible to perform *in situ* bioremediation of the unsaturated zone soil by inducing subsurface air flow as with soil vapor extraction, and by adding nutrients. In certain situations, biodegradation occurs naturally without nutrient addition.

An integrated systems approach must be taken to remediate a site with contaminated soil and groundwater. As shown in the left hand side of Figure 1, the groundwater table is lowered during groundwater pumping and treatment. This effectively increases the depth of the unsaturated zone, and thus can improve volatilization and capture efficiency of VOCs by the soil vapor extraction system. As shown on the right hand side of Figure 1, the groundwater treatment system will often be in operation during and after the unsaturated zone soil remediation is complete, and the soil vapor extraction system is removed. Note that bioremediation of soil or groundwater is not depicted in this figure.

A conceptual diagram for a soil vapor extraction system is shown in Figure 2 with activated carbon treatment of the extracted air prior to ambient discharge. Design considerations for a soil vapor extraction system are given in Table 2.

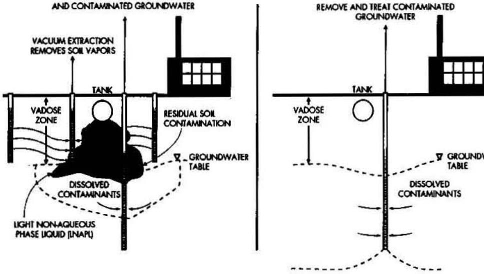

Figure 1. Integrated system approach to site remediation.

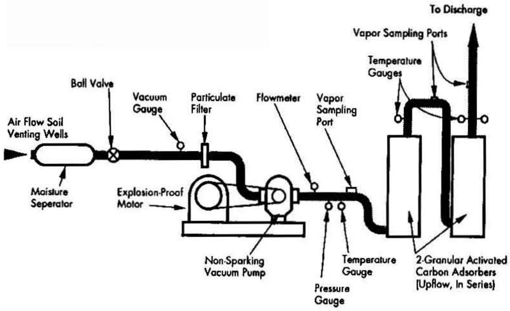

Figure 2. Conceptual diagram of soil vapor extraction and treatment equipment.

TABLE 2. DESIGN CONSIDERATIONS

Physical Site Constraints Above or Below Ground
Partitioning of Contaminants in the Vadose Zone Soils
Potential for Volatilization of Contaminants from the Groundwater and Subsequent Recontamination of Vadose Zone Soils
Potential Integration of Soil Vapor Extraction System with Enhanced Biodegradation and/or Groundwater Treatment
Optimization of Subsurface Airflow Pattern (Airflow Rate and Extraction/Injection Well Layout)
Off-Gas Treatment
Management of the Soil Vapor Extraction System
Remediation Time and Total Project Costs

REMEDIATION CASE STUDY

One example of a soil remediation project by soil vapor extraction is an ongoing (January, 1990) mandated remediation of soils contaminated with tetrachloroethylene (PCE) at an industrial facility in the Midwest. The soil contamination resulted from past industrial wastewater discharge to a network of leaching sumps. This practice was curtailed in the early 1980s when groundwater contamination was discovered near the site. The PCE-containing wastewater had leached from the sumps and infiltrated the soils, eventually reaching the groundwater table. From there, the groundwater transported the PCE off-site, forming a large contamination plume. Under a consent decree, the EPA mandated that the potentially responsible party (PRP) remediate on-site contaminated soils as part of the remedial solution to reduce future groundwater contamination.

ENSR investigated the extent of soil contamination with soil borings and a soil gas survey. Table 3 presents site characteristics which were determined to assess the feasibility of remediation by soil vapor extraction. These site characteristics were used to develop a conceptual model of the subsurface contamination, which was critical to design of the air extraction and injection well

TABLE 3. CASE STUDY—SITE CHARACTERISTICS

Size	40 ft × 75 ft (12 m × 23 m)
Area	3000 square ft (280 square meters)
Soil Volume	1500 cubic yards (1200 cubic meters)
Unsaturated Zone Depth	14 ft (4.3 m)
Contaminant: Tetrachloroethylene (PCE)	
Maximum Concentration	55 ppm
Average Concentration	13 ppm
Soil Type	Fine to Medium Sand Homogeneous and Isotropic
Soil Moisture	8.5%
Soil Porosity	0.35
Air Permeability of Soil	6.0E-7 square cm

TABLE 4. CASE STUDY—OPERATING CHARACTERISTICS

Vacuum Source	Single Vacuum Source
Well Vacuum	6 inch H_2O (15 cm H_2O)
Air Flow Rate	260 cfm (7400 liters/min)
Extraction Wells	6
Injection Wells	11
Impermeable Cap	Pavement—HDPE Liner
Monitoring	PCE Concentrations: Exhaust Gas, Soil Gas, Soil

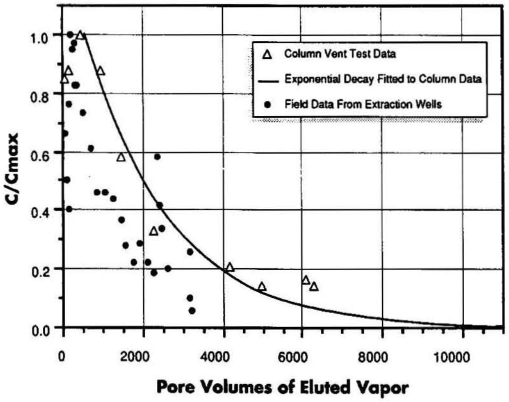

Figure 3. Case study tetrachloroethylene emission rate from laboratory column study and field data from soil vapor extraction.

system. In addition, state-of-the-art computer analyses of the subsurface airflow induced by the soil vapor extraction process were performed to select optimal locations for the wells [2]. Operating characteristics of the soil vapor extraction system are presented in Table 4.

To estimate the remediation time required to achieve the desired cleanup criteria of 1 ppm in the soil, a laboratory column study was performed [3]. A sample of soil taken from an area of the site containing the maximum amount of PCE was loaded into a laboratory soil column. A small airflow representative of the airflow rate achieved in a full scale soil vapor extraction system was passed through the laboratory soil column. The PCE emission rate was determined by measuring the concentration of PCE in the exhaust air from the column as a function of the pore volumes of air that had been eluted through the column (Figure 3). An exponential decay equation was fit to the laboratory data. As the site was relatively small and the on-site soils were homogeneous and isotropic, the modeled PCE emission rate curve from the laboratory column study was scaled-up to predict the PCE emission rate for the full scale soil vapor extraction system.

Average PCE concentrations at the site were determined from borehole soil samples. The laboratory-determined emission rate was used to estimate the total soil remediation time (five to six months at the given extraction rate) and the cost of remediation. ENSR also used this analysis to demonstrate to state regulators that the PCE emission rate during the predicted remediation period would not exceed the state air quality standards. Requirements for treatment of the extracted soil vapor were waived, reducing the cost of remediation for the PRP by approximately 15%.

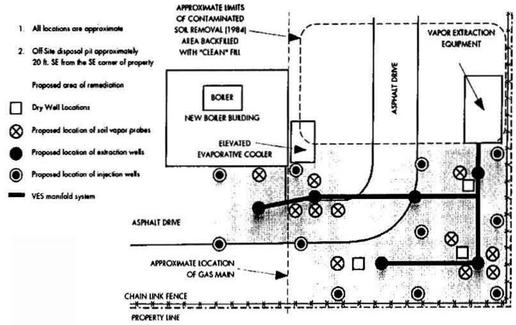

Figure 4. Case study site plan.

ENSR constructors installed the soil vapor extraction system and is implementing the soil cleanup (Figure 4). During cleanup, the subsurface vacuum, the in-ground soil PCE vapor concentrations, and the extracted air PCE concentrations are being monitored. A comparison of the actual extracted air PCE concentrations with predicted concentrations is presented in Figure 3. The field data in Figure 3 are the average PCE concentrations of the air extracted from the six extraction wells. The decay in PCE concentration in the extracted air from field operations parallels that of the laboratory column test. As expected, it is somewhat lower because the soil used in the laboratory column test was collected from the area of the site with the highest PCE concentrations. The spike in the field concentrations at 2500 pore volumes was due to a shift from equal extraction rates at all six wells to extraction at only the two wells with the highest residual concentrations.

CONCLUSIONS

Soil vapor extraction has found wide application for site remediation of VOC-contaminated soils. However, the subsurface airflow and contaminant transport processes are complex and not generally understood. Based on empirical analysis of the complex contaminant transport processes induced by the subsurface airflow using a laboratory soil column and subsurface airflow modeling, it is possible to provide an estimate of soil remediation time and cost at contaminated sites. Additionally, the feasibility of different remedial options in which soil vapor extraction might be used in conjunction with other technologies is more readily assessed using the approach described in this paper. This approach is well suited to small sites without excessive complexity due to heterogeneous and anisotropic soils or multiple contaminants. Where this is not the case, an *in situ* vacuum pump test may be more appropriate than a laboratory soil column test for determination of design data.

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In Situ Biodegradation of TCE Contaminated Groundwater

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Trichloroethylene (TCE) is one of the most widely used chlorinated solvents; it is also a common groundwater contaminant. TCE–contaminated groundwater is presently treated by transferring the solvent either to a solid (carbon adsorption) or to the atmosphere (air stripping). Biological treatment of the contaminated water is an alternative that causes complete destruction of the solvent. When performed within the aquifer it is termed in situ *biotreatment. A specific strain of bacteria (G4) has been isolated that degrades TCE enzymatically. The process has been extensively tested in the laboratory and confirmed in a field pilot test. The pilot test involved the injection of a clean, oxygenated water stream directly into the TCE plume. Nutrients and G4 were added to the injection stream and TCE concentrations were measured up–and downgradient of the injection well. A decline in TCE levels was observed eight hours after injection and continued for the following ten days. TCE concentrations were reduced from a high of 3,000 ppb to a mean value of 78 ppb during a 20 day period.*

INTRODUCTION

Trichloroethylene, commonly known as TCE, is one of the most widely used chlorinated solvents employed by industry. Its cleansing capabilities combined with its low flammability and lack of a measurable flash point have led to its wide-scale use in the metals processing, electronics, printing, pulp and paper, and textiles industries. Used primarily as a metals degreaser because of its ability to cleanse more thoroughly and efficiently than alkaline cleansers, TCE has been used for about 50 years worldwide. It is a colorless, volatile liquid which is classified as an RCRA hazardous waste. The maximum contaminant level allowed in drinking water is 5 parts per billion (ppb).

Cleanup technologies generally used for TCE-contaminated groundwater are air stripping and carbon adsorption. These processes do not eliminate the contamination; they simply transfer it to another medium. Increased restriction of air emissions is limiting the acceptance of air stripping of volatile organic compounds into the atmosphere, and disposal or regeneration of used

TABLE 1. SITE HYDROSTRATIGRAPHY

Hydrostratigraphic Unit	Description	Depth Below Grade (ft)
Upper Aquifer Zone	Brown silty sand (SM) interbedded with sand (SP)	0-40
	Sandy Clay (CL)	40-50
	Brown, coarse grained well sorted sand (SP) grading to gravelly sand	50-118
Clay Zone	Highly plastic, moist to dry brown clay (CL)	118-218
Lower Aquifer Zone	Coarse Sand (SP)	218-unknown

carbon, a hazardous waste, is costly. An alternative approach is to biologically destroy the TCE either in a surface bioreactor or within the contaminant plume.

BIODEGRADATION OF TCE

Bacteria (both aerobic and anaerobic) are the predominant life forms in groundwater aquifers [*1*] that survive in this environment by metabolizing low levels of residual organic substances which have migrated to the aquifer from overlying soils. A large proportion of these bacteria are aerobic species, such as coryneforms and pseudomonads, that are known to possess enzymatic pathways for the degradation of a wide range of organic compounds.

A bacterium was isolated that decreased TCE concentrations in initial batch studies from 460 ppb to below detectable levels (<2.6 ppb) overnight [*2*]. The bacterium was identified as a strain of *Pseudomonas cepacia*, designated strain G4, and was shown to degrade TCE cometabolically when induced for the degradation of phenol or toluene [*3*]. *Pseudomonas* species represent bacteria typically found in soils and water. Later studies achieved biodegradation of TCE at concentrations up to 20 ppm. Experiments performed with [U-^{14}C]-TCE indicated 60 percent of the carbons present in TCE are converted to CO_2, with 57 to 78 percent of the remaining carbon being associated with cell material. The data demonstrated the bacterial system completely degraded TCE to CO_2 and cell assimilated carbon. The complete biological detoxification of TCE was further confirmed by dechlorination studies, which indicated complete conversion of the chlorines of TCE to innocuous inorganic chloride ions.

A survey of six strains of bacteria known to degrade aromatic compounds identified two other microorganisms that degraded TCE. Two strains of *Pseudomonas putida* that degraded toluene also degraded TCE. In addition, the natural microflora in water samples from an aquifer, an estuary and a river were all stimulated to degrade TCE when exposed to phenol or toluene. The results indicate that a number of microorganisms are capable of degrading TCE when exposed to certain aromatic compounds. Therefore, these types of organisms would be expected to be part of the natural microflora at TCE–contaminated sites. Strain G4 has also been tested for its ability to degrade other volatile chlorinated aliphatic compounds

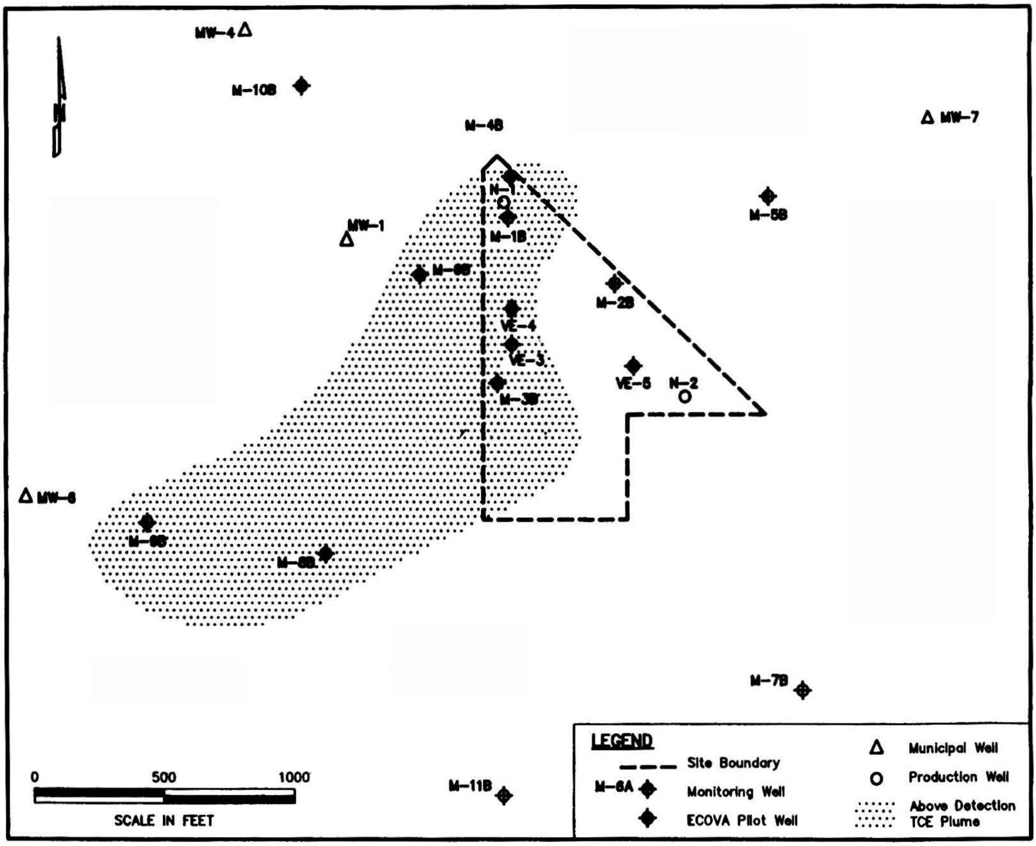

Figure 1. Upper Aquifer, shallow hydrochemistry.

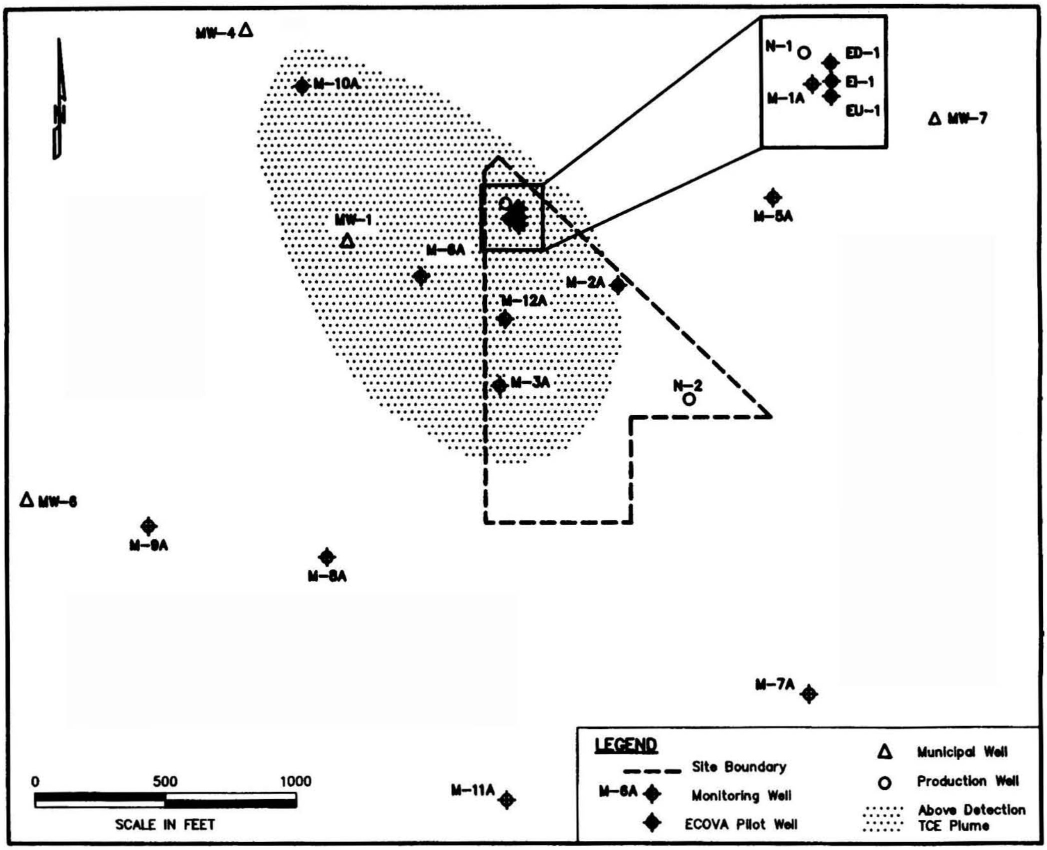

Figure 2. Upper Aquifer, deep hydrochemistry.

based on production of Cl or disappearance of the parent compound. The results indicated strain G4 was able to degrade *cis* and *trans*-1,2,-dichloroethylene, 1,1-dichloroethylene and vinyl chloride.

IN SITU TREATMENT TECHNOLOGY

In situ bioremediation involves the controlled management of microbial subsurface processes [*4*]. An understanding of the biodegradation of the target contaminants and the site hydrogeology are required. *In situ* systems generally utilize aerobic processes and involve the introduction of oxygen, nutrients and sometimes specific microorganisms to the subsurface. Two key criteria for *in situ* treatment are 1) a permeable matrix to allow rapid oxygen and nutrient transport and 2) contaminant degrading microorganisms. *In situ* treatment systems involve either: a) pumping the contaminated groundwater to the surface from a downgradient recovery well, passing it through a surface treatment unit, amending it with nutrients and oxygen and reinjecting it into the subsurface via an upgradient injection well; or b) directly stimulating microbial activity in the aquifer via direct injection. The *in situ* bioremediation of TCE contaminated groundwater was performed using approach (a).

SITE HYDROGEOLOGY

A California manufacturing facility utilized TCE in its production process; an RCRA monitoring well system detected TCE in groundwater beneath the site. Detailed site investigations identified three major hydrostratigraphic units: 1) Upper Aquifer Zone, 2) Clay Zone and 3) Lower Aquifer Zone. A description of each zone and further subdivisions is provided in Table 1.

Local domestic wells tap the shallow permeable unit of the Upper Aquifer. Larger capacity wells (such as the plant production well) draw water from the deeper, more permeable unit of the Upper Aquifer. The Clay Zone acts as a low permeability aquitard between the two aquifers, although it does contain seams of water-bearing sand.

GROUNDWATER FLOW AND QUALITY

Groundwater in the Upper Aquifer flows horizontally in a northwest direction beneath the site under an average gradient of 8×10^{-4} ft/ft. In addition, there is significant downward vertical groundwater flow from the shallow silty sand to the thick gravelly sand unit. Average downward gradients range from 1 to 4×10^{-4} ft/ft, and represent a significant component of groundwater flow beneath the site.

The shallow and deep units of the Upper Aquifer contain above background concentrations of TCE. The sand layers within the Clay Zone also contain detectable quantities of TCE. Although the source has been removed, the TCE plumes in the Upper Aquifer have become widely dispersed. This is a result of the hydraulic connection between the two permeable units, rapid groundwater velocities, and variation in regional flows.

Figures 1 and 2 illustrate TCE plume geometries in both permeable units of the Upper Aquifer. Each plume

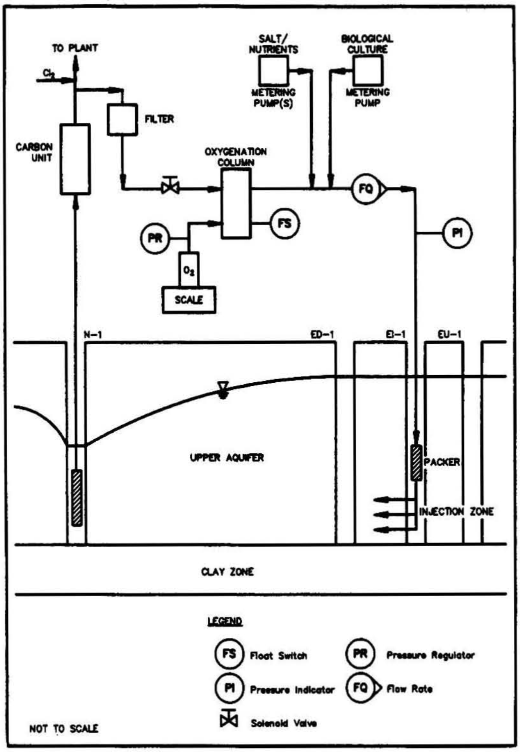

Figure 3. Pilot program process flow diagram.

covers an area of approximately 30 acres; the shallow plume extends to the southeast of the site while the deeper plume has spread to the northwest. From the distribution of TCE concentrations it is believed that the heavier-than-water TCE moved vertically downward under gravity as a dense non-aqueous phase liquid (DNAPL). During its descent, the DNAPL became diluted and dissolved initially within the upper permeable unit and with time into the deeper sand and gravel layers. This mixing was facilitated by the strong natural gradients that had developed as a result of the high permeability and pumping.

PILOT SYSTEM DESIGN

To test the feasibility of *in situ* biodegradation of TCE it was decided to conduct the pilot program in close proximity to an active withdrawal well, in this case the plant production well N-1. This well withdraws up to 200 gpm from the lower unit of the Upper Aquifer and develops rapid groundwater flow velocities in its vicinity. An injection well (EI-1) and up–(EU-1) and downgradient (ED-1, M-1A) monitoring wells (10 feet away) were installed for the test program. The insert (Figure 2) shows the locations and layout of the test wells.

The *in situ* system was set up as illustrated in Figure 3. A tapline, installed downstream of the N-1 carbon unit, conveyed water to an aeration column, a nutrient/bacteria feed system and into the lower permeable layer of the Upper Aquifer via injection well EI-1. To ensure a maximum feed rate, the delivery zone was vertically restricted by means of an inflatable packer. Dedicated, submersible, air-driven sampling pumps were installed in monitoring wells ED-1 and M1-A.

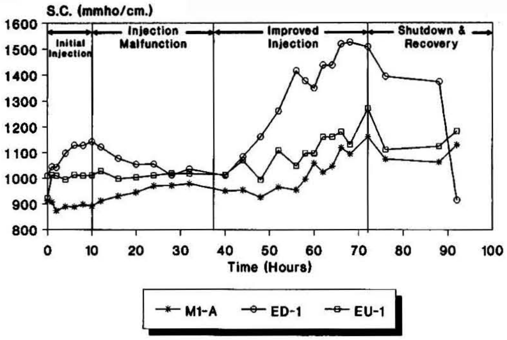

Figure 4. Tracer test conductivity profiles.

A two-phased pilot program was implemented for the *in situ* biodegradation of the TCE plume. Phase One involved the injection of TCE–free water containing a sodium chloride tracer into the aquifer to quantify the effects of dilution on groundwater TCE concentrations. Phase Two involved the injection of oxygen, nutrients, and G4 into the aquifer to quantify the effect of *in situ* microbial degradation of TCE.

PHASE 1-TRACER TEST

The tracer test was performed to determine a) groundwater velocity in the lower permeable unit of the Upper Aquifer and b) the effect of dilution on TCE concentrations. To achieve these goals, a tracer was introduced into the injection well (EI-1) and monitored in the surrounding wells (ED-1, M1-A and EU-1).

An ideal tracer [5] should:

- be susceptible to quantitative determination in minute concentrations
- be absent, or nearly so, from the natural water
- not react chemically with the natural water or be absorbed by the porous media
- be safe in terms of human health
- be inexpensive and readily available

To satisfy these criteria, water–softening salt (sodium chloride) was selected as the tracer; an increase in specific conductance in the monitoring wells would indicate the migration of the tracer. The saline solution was fed to the water stream that was injected into the well at a rate of 7,200 gallons/day (5 gpm). Before starting the test, baseline conductivity measurements were taken in the three monitoring wells. The tracer test was initiated on August 21, 1989. Water samples were collected at 2-hour intervals for the first 12 hours and then every 4 hours until 36 hours after initiation (Figure 4). The samples were tested for conductivity, temperature and dissolved oxygen at each well-head. At the same time, 40 ml vial samples were taken and sent to the on-site laboratory for TCE analyses (EPA method 601).

The initial saline feed system never achieved more than 50% of the required rate of 30 gallons/day. This condition was corrected by replacing the saline feed pump with a direct-feed gravity flow line connected downline of the injection pump. A second injection with the improved system began approximately 38 hours from the time of original test initiation. Figure 4 clearly demonstrates the response of the increased saline delivery rate. The test was terminated August 24, 1989, after the tracer had been detected in the two downgradient wells (ED-1, M1-A) and the upgradient well (EU-1). Conductivity values continued to be taken after saline injection was discontinued.

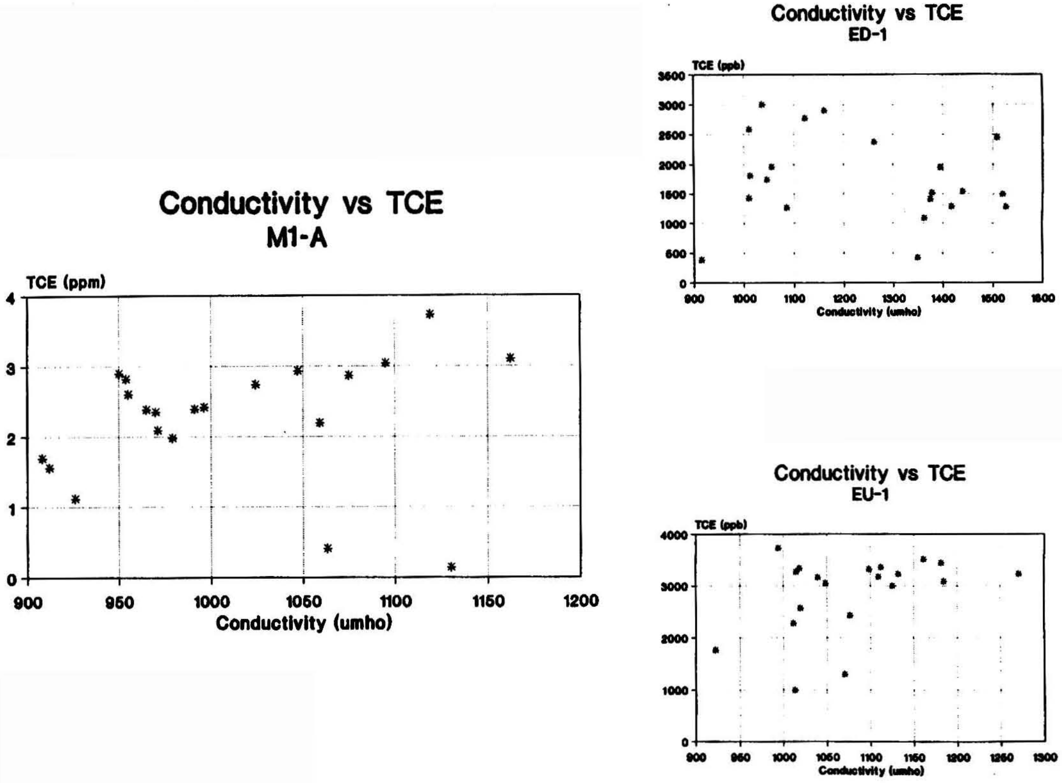

Figure 5. Conductivity versus TCE.

Groundwater velocity in the lower permeable unit was calculated to range between 2 and 5 ft/hour. This was determined by dividing the time taken for the first occurrence of tracer at the two downgradient wells by their respective distances from the injection well.

TCE Dilution

The issue of dilution is a key point in verifying the validity of the *in situ* biotreatment process. TCE values were plotted versus conductivity to determine if there was a correlation between TCE and salt concentration. An increase in conductivity would parallel the ingress of the injected water. If the freshwater injection was diluting the contaminated groundwater then a decrease in TCE levels could be expected to correspond with an increase in conductivity. By plotting the two parameters a negative correlation (*i.e.*, declining TCE values versus increasing conductivity values) would have been proof of dilution. Some correlation appeared in well ED-1, but not wells M1-A or EU-1 (Figure 5).

By calculating the daily flow of groundwater in the injection zone and comparing it with the amount of water injected, it should be possible to calculate the expected dilution effect. The receiving zone had a saturated thickness of 14 ft. and a width of 20 ft. (minimum, based on the appearance of tracer at all monitoring wells), an effective porosity of 25% and a flow velocity of 48 ft./day. Based on these data approximately 25,000 gallons/day (gpd) were flowing through the receiving zone. By comparison, the injection stream was run at a steady rate of 5 gpm (7,200 gpd) representing 29% of the flow into which it was placed. Based on this calculation, a 30% decline in TCE levels could be ascribed to dilution.

We believe that during the initial stages of injection, some dilution and hence reduction of TCE values was occurring in well ED-1. No evidence of dilution was seen in wells EU-1 or M1-A. By contrast, the overall reduction (95%) in TCE values achieved during the subsequent biological test far exceeded the effects of dilution.

Temperature and Oxygen

Throughout the tracer test, groundwater temperature and dissolved oxygen were measured at the same time the conductivity and TCE values were recorded. Temperature values within the three wells coincided with each other, fluctuated between 19°C and 25°C, and followed the diurnal cycle. Dissolved oxygen levels varied from 3 to 5 ppm throughout the tracer test. These relatively high natural oxygen levels together with the fluctuating groundwater temperatures would indicate connection and recharge of the deep unit with shallow, near–surface ground and/or surface water.

PHASE 2-BIOTREATMENT TEST

The *in situ* treatment system utilized the same injection and monitoring wells and the same injection rate (5 gpm) as the tracer test. Injection of recharge water began on Wednesday, September 6, 1989. Nutrient feeds were initiated the following day and terminated Wednesday, September 13. Various additions were made to the recharge water to stimulate degradation of TCE. The water was oxygenated and both inorganic and organic nutrients were introduced into the feed. In addition, a culture of strain G4 was added during the initial phase of the test. Nutrients and oxygen were added continuously for 6 days.

Table 2. Range of Oxygen Concentrations During the Pilot Treatment

Well	Oxygen Concentration (ppm)	
	Min	Max
ED-1	4.0	14.6
M1-A	4.0	12.3
EU-1	2.8	12.5

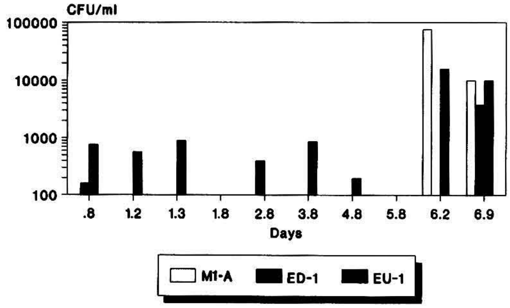

Figure 6. Plate counts for enumeration of strain G4 in monitor wells.

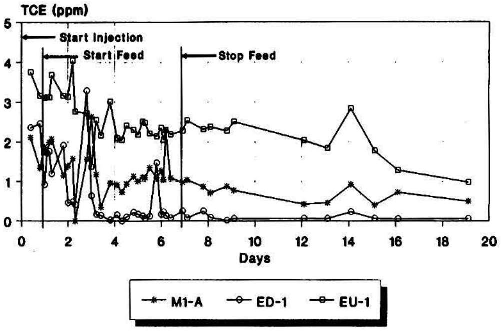

Figure 7. *In situ* TCE degradation.

Oxygen Concentrations

The addition of oxygen to the feed maintained high levels of oxygen downwell during the test period, ensuring the necessary aerobic conditions for the treatment. The range of oxygen concentrations from initiation of the test to termination of feed ($T = 166$ h) is summarized in Table 2 for the three monitoring wells. As expected, as treatment continued and microbial activity was expected to increase, the oxygen levels decreased. However, at no time did oxygen concentrations decrease to levels approaching anaerobic conditions.

Microorganisms

The monitoring wells were periodically tested for the presence of strain G4 using a semi-selective plate count method (Figure 6). Before injecting the G4 strain (0.8 days; Figure 6) initial tests showed low levels (10^2 to 10^3 cfu/ml) of strain-G4-like microorganisms in wells ED-1 and EU-1, respectively, and $<10^2$ cfu/ml (detection limit) in M1-A. Another test (6 hours after injection, 1.2 days) showed 5.7×10^2 cfu/ml in well EU-1 and $<10^2$ cfu/ml in

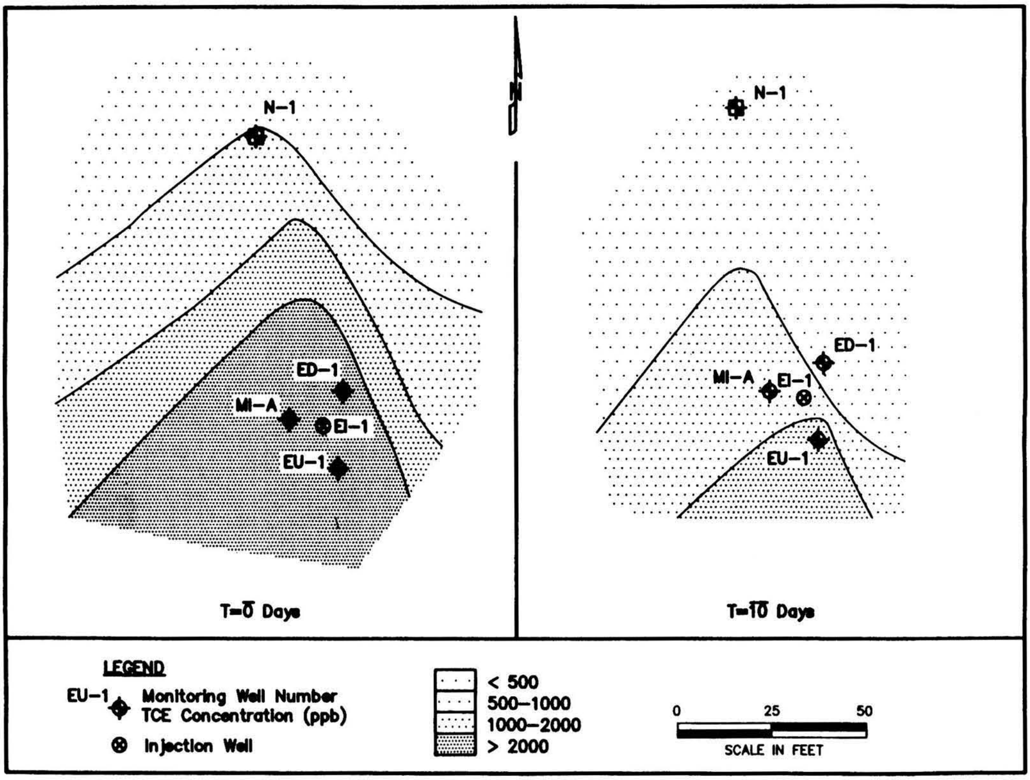

Figure 8. Before and after TCE plume.

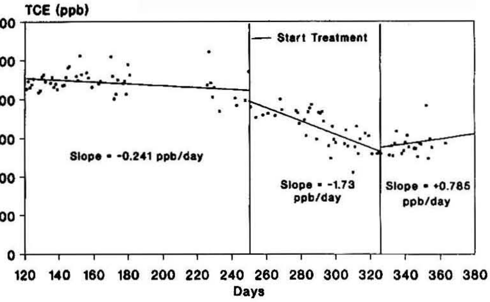

Figure 9. TCE concentration trends in production well N-1 before and after treatment.

both ED-1 and M1-A. These results indicate that very low levels of strain–G4-like microorganisms were already present in the aquifer. Any organisms observed at these two time points can be considered as naturally occurring and not representing the inoculation of strain G4. The results for the following 5 days indicate $<10^3$ cfu/ml of organisms in all three monitoring wells.

Thus, the inoculation of strain G4 did not result in a detectable increase at the monitoring wells for 5 days. This does not exclude the possibility of higher numbers of the microorganisms being present in the aquifer, but closer to the point of injection (*i.e.*, <10 ft from EI-1). An increase in G4-like microorganisms was first detected at $T = 6.2$ days, and was 7.6×10^4 and 1.6×10^4 cfu/ml in wells M1-A and EU-1, respectively. Similar results were obtained at $T = 6.9$ days, which was the final test for microorganisms. In this instance all three wells showed significant levels of microorganisms. Wells ED-1, M1-A and EU-1 contained 3.8×10^3, 1.0×10^4 and 1.0×10^4 cfu/ml, respectively at 6.9 days. The significant increase in microorganisms observed in these last two points most likely represent migration of strain G4 from the point of injections outward to the three surrounding wells. The production well N-1 was tested at these last two time-points and showed less than 10^2 cfu/ml. Thus, no detectable levels of strain G4 had migrated as far as the production well (ca. 75 ft from injection).

TCE Disappearance

After 24 hours of feed ($T = 2$ days), TCE concentration in the downgradient well (ED-1) had dropped from 2500 ppb to 466 ppb (Figure 7). It remained in this concentration range for the next 8 hours. The following morning ($T = 2.8$ days) the concentration had increased to 3280 ppb in ED-1. Difficulty with the pump feed for the organic nutrients was also observed about this time. Inadequate carbon feed may have been responsible for the increased TCE level, but this cannot be conclusively established. Within the next 8 hours the concentration fell below 200 ppb and, with the exception of one data point ($T = 5.8$ days), all subsequent concentrations were below 300 ppb. The mean and standard deviation for the data from 3.1 to 8.1 days (5-day interval), excluding $T = 5.8$ days, was 135 ± 72 ppb ($n = 19$). We continued to monitor TCE concentrations, and subsequent readings showed a further decrease in TCE. The mean and standard deviation over the next 10 days ($T = 8.8$ to 19.1 days) was 78 ± 64 ppb ($n = 8$).

Decreases in the concentration of TCE also occurred in wells M1-A and EU-1. The time of response was longer and the magnitude of the decrease was less than observed for ED-1. M1-A showed the decrease next, about 1.5 days after feed initiation ($T = 2.5$ days) and dropped from 2,000 ppb to a mean concentration of 572 ± 205 ppb ($n = 6$) for the last 7 days ($T = 12.1$-19.1 days). A decrease in TCE was subsequently observed in well EU-1 after 2 days of feed. The concentration in this well dropped from approximately 3,000 ppb to a mean concentration of 1,809 ± ppb ($n = 6$) for the last 7 days. These results were consistent with the results of the tracer studies, which showed the most rapid communication between the injection well (EI-1) and well ED-1, followed by well M1-A and finally the upgradient well (EU-1).

The data indicate a substantial decrease in TCE resulting from the pilot treatment; Figure 8 summarizes before and after test plume configurations. The effect of treatment continued after termination of the feeds. This is consistent with the plate-count data, which showed strain G4 did not reach the monitoring wells until the day before termination of feeds. Finally, Figure 9 illustrates the sharp decrease in TCE concentrations in production well N-1 before and after the test.

CONCLUSIONS

The *in situ* biodegradation of TCE–contaminated groundwater was successfully demonstrated at the pilot scale.

A sodium chloride tracer was introduced into the injection well at a rate of 5 gpm. Groundwater samples were collected and their conductivity measured on a frequent basis, both up–and downgradient of the injection well, to monitor the spread of the tracer.

The tracer test confirmed that the injection water spread up–and downgradient of the injection well and that groundwater flow velocities within the receiving zone were on the order of 2 to 5 ft./hour. A theoretical dilution of TCE concentrations was calculated based on the ratios between the rate of injection and the flowrate of the receiving zone. Measurable dilution effects were only observed in the downgradient well.

The tracer test was followed by the introduction of TCE–degrading bacteria, organic and inorganic nutrients, and oxygen into the lower permeable unit of the Upper Aquifer over a six-day period. Within eight hours of initiation, a measurable decline in TCE concentrations was observed. A corresponding decline in oxygen levels was observed, suggesting that microbial degradation had been activated.

The *in situ* test demonstrated biological degradation of TCE–contaminated groundwater from a high value of 3,000 μg/l to a mean concentration of 135 ppb, which was maintained from day 3 to day 8. A further decline to a mean value of 78 ppb was observed over the next 10 days.

The pilot test proved that TCE can be removed from groundwater by *in situ* aerobic biodegradation. The rapid reduction rates are very encouraging as they indicate that under the right conditions, the contaminant plume can be significantly reduced within a short time frame.

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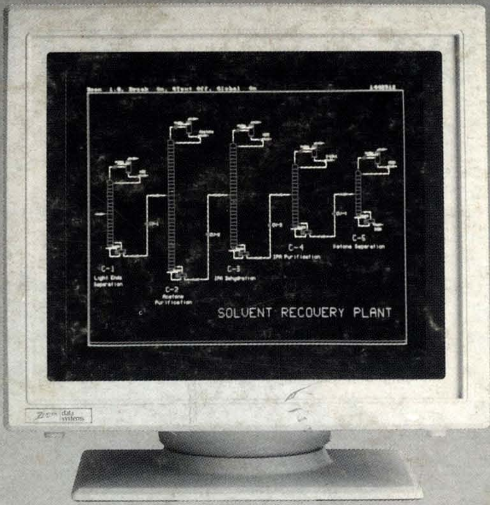

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