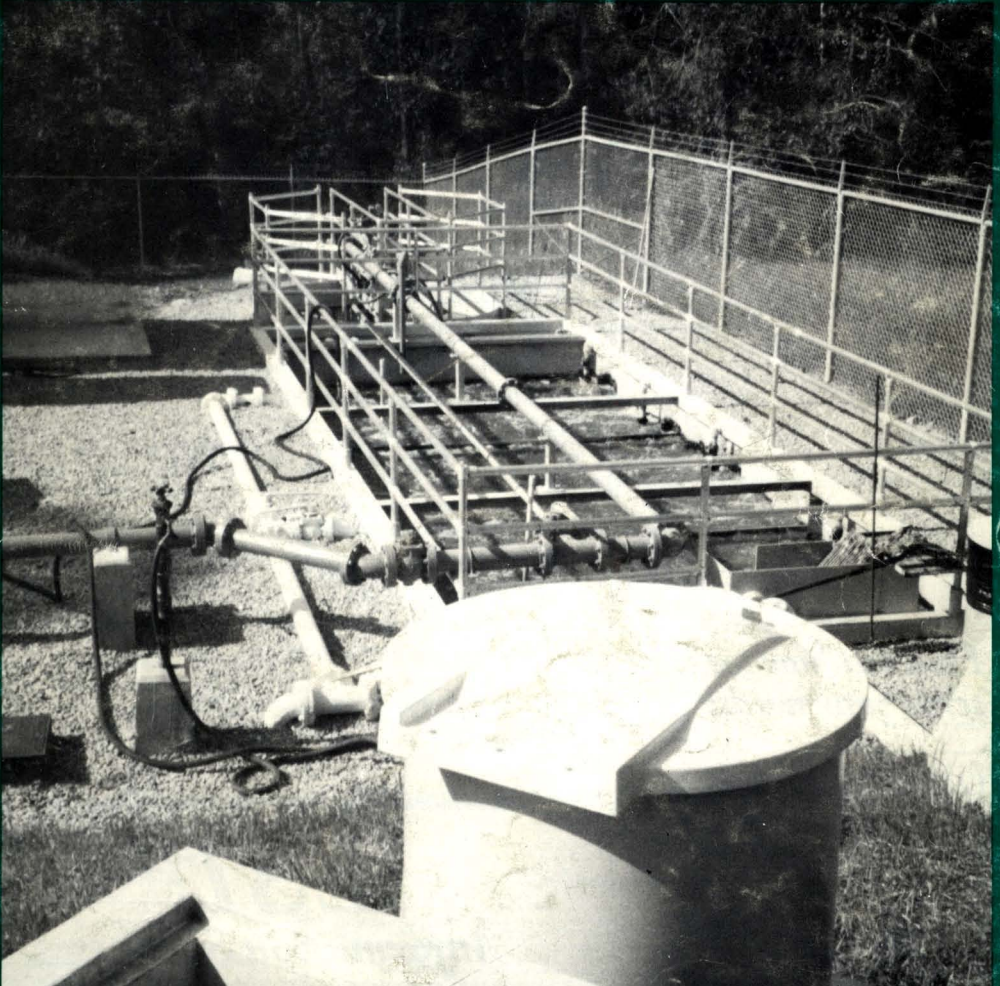# ENVIRONMENTAL PROGRESS

The Fixed Activated Sludge Treatment System (FAST®) is an aerobic, fixed film, packed bed reactor with 100% submerged media. Photo courtest of Smith & Loveless Inc., Lenexa, KS.

ENVIRONMENTAL PROGRESS

Contents

Environmental Stewardship: It's Good Business

Robert v.d. Luft

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Among the many factors critical to the success of today's businesses, one of the most important is our ability to operate in an environmentally sound manner. It has been, and will continue to be, an uphill struggle.

Although corporations have made significant progress during the past several years, many groups promote a stereotype in which industry forever exists in a kind of fallen state with regard to the environment. This stereotype suggests that everything a company does is motivated by the need for profit. The implication is that corporate environmentalism is "greenwash" and that it is hypocritical to declare our environmental commitment and to call attention to the progress we are making.

How did industry aquire this reputation? Three factors are involved: the first one is *scale*. Industrial environmental problems, whether actual like the Valdez spill or apocryphal like the "Alar" scare, grab headlines. These headlines are far more visible than the non-point source pollution from millions of households or automobiles.

The second factor is corporate policy *inertia*. This inertia has allowed many environmentally detrimental industrial practices and attitudes to continue - even after we realized there are better ways of doing things.

The third factor is *rhetoric*. Due to factors one and two, industry is cast as the environmental "bad guy" by activists and politicians. Companies, unfortunately, often

live up to this image by the way in which they respond to real problems and legitimate concerns.

Our goal is to change this negative reputation. The advantage of a market economy in a democratic society is that, sooner or later, industry *does* respond to public demands for that which is safer or cleaner. This is what is happening in the U. S. right now and elsewhere in the world.

During the next quarter-century the most significant net contribution to a greener world will be made by industrial corporations. Governments can regulate. Environmentalists can agitate. But only industry can innovate. The processes and products that will enable us to continue to experience economic prosperity, to enjoy high standards of living and, at the same time, to have a sound ecology will come from industry. The green economies and lifestyles of the 21st Century may be conceptualized by environmental thinkers. They can, however, only be actualized by industrial corporations.

Smokestacks and waste pipes are where we have traditionally focused our attention in complying with environmental regulations. We're now taking a different view of what's going up the stacks and out of the pipes. We don't think of it as waste, but as potentially viable co-products. These co-products can be captured and put back into the system - preferably before emission. Or they can be sold as viable products on their own merits.

In the 1970s and most of the 1980s, the criteria for waste stream conversion to specialty chemicals was based on economics. How much value does this material have in

the market place relative to our cost to produce it?

Accelerated commitment to environmental improvement has prompted us to rethink our criteria.

In the mid-1980s we began to evaluate our streams by the following criteria: first, we looked at the streams that were likely to be subject to future legislation or regulation, either for human health or environmental reasons. Finding markets for those streams became a top priority. Second, we reviewed stream size. Obviously, we prefer to spend time seeking a market for a large stream rather than a small one. We also reviewed market potential, ease of replacement for existing products, and opportunities to add superior value to customers. The key difference between our business today and 20 years ago, is that the environmental solution is dialed into the equation up-front. The return we are willing to accept for one of these streams is balanced against the avoided cost of disposal.

Nowhere in our environmental goals and actions are there statements of ethics. However, these commitments flow from an unmistakable ethical framework. There are four ethical responsibilities that underlie our environmental policies, goals and actions.

First, *minimize the environmental impact of everything we do* consistent with our obligations to our stakeholders.

This is perhaps the most important ethical tenet that a corporation can adopt in deciding its environmental policy. A lot of industrial environmental problems could be solved tomorrow - if we didn't have customers, employees, shareholders and obligations to society. Du Pont could have saved itself a lot of grief if, when presented with data linking CFCs to atmospheric ozone depletion, we simply pulled the plug on our CFC business. Of course, we would simultaneously have pulled the plug on your refrigerator and air conditioner and on some $200 billion worth of equipment worldwide that requires CFCs.

We don't apologize for taking the concerns of our customers and employees and the needs of society into consideration when we decided to orchestrate an orderly phaseout of these materials rather than a traumatic shutdown. In fact, we believe that we are ethically and legally obliged to do so.

The second underlying ethical principle of our environmental policy is *consider the ultimate disposition of everything we produce.*

Everything we make ends up somewhere, and those "somewheres" are becoming increasingly hard to find. Less than a century ago any waste - private, government or industrial - could be put in just about any hole in the ground, body of water, out-of-the-way field or pumped into the air. As a society, we didn't consider where a product would end up after its useful life was over. We didn't generally consider recycling or reusing products.

All that has changed. Now ethically we must give thought to where a product will end up after it has served its purpose. This is especially crucial for products that have toxic properties or which can break down into toxic materials. It is also true of useful products like plastics that are inert and can remain intact for decades to centuries.

The third ethical principle that guides our environmental policy is: *reduce volumes of energy and raw materials used while creating prosperity.*

Creating prosperity has always been considered a benefit of industrial development. But traditionally the creation of prosperity has assumed that resources for development would always be available somewhere on the globe. We also assumed that the earth could absorb the by-products of industrial societies indefinitely. Those assumptions no longer hold. We now accept that ethically we cannot use energy and raw materials with abandon. We cannot destroy ecosystems on which the well-being of the present and future generations depend.

This means we have to accept that industrial progress in the future will come in the form of sustainable development, rather than along the traditional model in which the environmental degradation was not a compelling factor in our economic decisions. Sustainable development means taking care of the needs of all the world's people today, without depriving future generations of the resources or the environmental integrity they will require tomorrow.

The fourth ethical principle that helps us determine environmental policy at Du Pont is *dialogue to minimize fear and increase understanding.*

The traditional image of industry, especially the chemical industry, is that what went on within the plant fence was nobody's business. As the public became aware of environmental concerns in recent years, this attitude led to mistrust, fear and misunderstanding. The chemical industry has changed its approach and has undertaken a broad program - Responsible Care - to share with the public what goes on inside chemical plants, the properties of the materials we use and make, and potential dangers and hazards.

Inherent in our efforts to share is an obligation to listen - to engage - to dialogue. We must invite members of the public into our facilities. To see us is to know us; knowing us starts the process of building trust. It's a continuous process. And the communication must always be two-way. At Du Pont, we have community advisory committees at a number of our sites. These committees act as a sounding board, a counselor, a reality check. Not to have them is risky - for they are a pathway to the public consent we need to operate.

If industry were to test all of its policies against these four ethical imperatives, we will have gone a long way toward creating an industrial culture that is responsive to value for the environment. That's the challenge. That's the opportunity. And yes, it's also good business.

Louis J. Thibodeaux Receives Environmental Division Award

Louis J. Thibodeaux has received the AIChE Environmental Division's Lawrence K. Cecil Award in Environmental Chemical Engineering. Thibodeaux is Jesse Coates Professor of Engineering and director of the U.S. Environmental Protection Agency-sponsored Hazardous Substance Center South/South-west at Louisiana State University (LSU). Given to "recognize outstanding chemical engineering contributions and achievements toward the preservation or improvement of the natural environment," Thibodeaux received the award during ceremonies at the AIChE Summer National Meeting in Minneapolis last August.

Thibodeaux has been on the LSU faculty since 1984. Last year he was a visiting professor at Ecole Nationale Supérieure des Mines de Paris, Centre d' Information Geologique in Fontainbleau, France.

Before returning to LSU, where he earned a bachelor's degree in petroleum engineering and master's and doctoral degrees in chemical engineering, Thibodeaux served on the faculty of the University of Arkansas for 16 years. During this period, his research interests in environmental matters moved from wastewater treatment to environmental chemodynamics. His teaching interest was in the same vein, and a course and textbook followed. The textbook - *Chemodynamics* -

Environmental Movement of Chemicals in Air, Water, and Soil, is used in senior and graduate-level courses at universities nationwide. In 1982, the University presented him its Alumni Award for distinguished teaching and research.

Thibodeaux has published more than 100 articles, served as a consultant to a variety of companies and government agencies, and is a member of the editorial boards of several publications including the *Journal of Hazardous Materials, Hazardous Waste and Hazardous* Materials, and the *Journal of Toxicological and Environmental Chemistry.* He has also served as chair of the Environmental Division.

Fast, Cheap Oil-Spill Cleanup Method Reported

A way to clean up a Valdez-size oil slick in three days at a fraction of the cost was described recently by a National Science Foundation (NSF)-funded chemist at the American Chemical Society's national meeting in San Francisco.

Adam Heller, James R. Bock, and others at the University of Texas chemical engineering department in Austin, said they have developed in the laboratory a method for treating oil slicks on seawater so the sun can dissolve them in a matter of days. Sunlight is used instead of detergents to help bacteria in the water biodegrade the oil.

The chemists attached photocatalytic particles of palladium-activated titanium

dioxide, a nontoxic pigment used in white paint, to tiny, hollow glass beads that allow the photocatalysts to float on top of an disperse the oil. There are two types of beads: one maximizes spreading of the photocatalysts over the spill. This type stays with the spill, efficiently harvesting sunlight and thereby accelerating dissolution of the oil. The other is designed to treat spills that imminently endanger shores or marine life. This type soaks up the oil and forms floating clumps (aggregates), which slowly disintegrate into white sand-like particles as the oil photooxidizes in sunlight, Heller explained. The beads are the same diameter as a human hair.

"We estimate that upon exposure to 10 hours of sunlight a day, a Valdez-size slick might be 'photo-solubilized' in two weeks - at a cost of about one percent of that of the Valdez cleanup, and in three days at a cost of about five percent if treated more heavily," Heller reported. "The cleanup costs that Exxon charged were $1.89 billion in 1989 and $2 billion in 1990."

The chemist emphasized that his estimates are based on laboratory-scale experiments. He said both the titanium dioxide and the aluminosilicate glass beads are relatively inexpensive, with the latter selling as "filler" for 50 to 70 cents per pound.

Waste Reduction Center Releases Student Homework Manual

AIChE's Center for Waste Reduction Technologies (CWRT) has released *Pollution Prevention: Homework & Design Problems for Engineering Curricula,* to increase concepts that should become a permanent feature of industrial practice.

CWRT believes that by incorporating cost-effective pollution prevention technologies and methodologies into standard engineering curricula, students will learn to integrate environmental considerations into their decisions, becoming "pollution prevention" engineers.

The American Institute for Pollution Prevention contributed case studies, crafted as multi-disciplinary problems, that embody chemical and materials engineering principles. In publishing this homework manual, CWRT aims to make undergraduate engineering students aware of the professional and ethical responsibilities they'll have as they develop the next generation of clean process technologies.

Pollution Prevention: Homework and Design Problems for Engineering Curricula is designed to be integrated into existing courses leading to chemical and other undergraduate engineering degrees, ranging from sophomore-level material balances to senior-level process design. It may also be used by graduates beginning industrial careers, and with industrial in-plant courses to stimulate engineers' creative problem solving abilities.

This reference manual contains over 20 problems, their solutions and questions for discussion. The book is well illustrated with many charts, tables and graphs.

The 155-page paperbound edition is available for $35 (international $49) from AIChE's Publication Sales Department, 345 E 47th St., New York, N.Y. 10017. Telephone: (212) 705-7657; FAX: (212) 752-3294.

CWRT Sponsors Pollution Prevention Workshop for Government Permit Writers

The Center for Waste Reduction Technologies and the EPA's Pollution Prevention Division and Office of Cooperative Environmental management are cosponsoring a workshop on pollution prevention training for government permit writers, and rulemakers. The workshop will be held on December 3, and 4, in Washington, D.C.

This workshop will provide government officials with a better understanding of how the refining and chemicals processing industries identify opportunities to employ waste reduction techniques and technologies to comply with current and emerging regulations. The workshop will emphasize opportunities to apply initiatives within the context of permit writing and analysis. A special focus of the workshop will be the new requirements and permits called for under the Clean Air Act Amendments of 1990 (CAAA).

The target audience, limited to 40, is EPA and state personnel, especially those responsible for permits under the CAAA. The workshop will include breakout sessions to systematically evaluate specific plan/process configurations and operations for missed pollution prevention opportunities among other topics.

There is no charge to attend the workshop. For more information, please contact Tammy Nilson, at the Center for Waste Reduction Technologies, AIChE, 345 E 47 St., New York, N.Y. 10017. Telephone (212) 705-7424; FAX: (212) 752-3297.

Emissions from Combustion Processes: Origin, Measurement, Control, Raymond Clement and Ron Kagel, editors. Lewis Publishers, Inc., Chelsea, MI, 491 pages [ISBN No:0-87371-172-6] U.S. List Price: $ 69.95 (1990).

This book, a very timely one, reports on research on the environmental aspects of combustion. The book contains 31 contributed chapters. Most of the chapters, despite the broad title of the book, are directed towards incinerator emissions and this is one of the book's most useful characteristics. The other useful feature is that the editors have successfully brought investigators with different expertise in incinerator emissions together in a convenient compilation. The fact that one can read about the basic chemical processes involved in dioxin formation, the measurement of these toxic chemicals in the laboratory and in the field, their transport and fate in the environment and the associated risk assessment analysis in one handy source is enough of a reason to buy this book.

An overview of conventional combustor emissions in the U.S., is given in Chapter 1. Although the information provided is useful, it only relies on EPA publications and is a bit outdated. For example, most of the emissions data extend only to 1980-1985, rendering their extrapolation to present time somewhat questionable.

Chapters 2 through 8 and 19 deal with various chemical and physical processes associated with the formation of toxic combustion by-products, such as chlorinated dioxins and furans, and their control. These are some of the more scientific sections of the book, and provide the reader with a fine summary of the state-of-the-art in this subject. For the scientifically oriented reader, these are the chapters not to be missed.

The acquisition of unambiguous data on trace combustion by-products is crucial to assess pollutant emissions from incinerators, and Chapters 9 through 11 address various issues related to such measurements. The importance of data quality, such as, accuracy and precision, quality assurance, and isotope tracer techniques are discussed.

Chapters 13 and 14 deal with various technical and non-technical issues related to the practical implementation of the incinerator technology. Technical issues that require additional research as well as several common misconceptions about incinerator technology are described in these chapters.

The application of several measurement and testing techniques to characterize the emission behavior of several specific combustion/incineration devices (such as, steel foundry, rotary kiln) are the subjects of Chapters 15, 16, and 22 through 24. The experience from the Canadian National Incinerator Testing and Evaluation Program are also reported in Chapters 17 and 18.

The control of sulfur and nitrogen-containing pollutant emissions from combustion sources are discussed in Chapters 20 and 21. These chapters provide a somewhat different pace to the book, but are not distracting from the main flow which is trace toxic pollutants.

The transport and fate of toxic trace pollutants in the environment are the subjects of Chapters 26 through 28. Processes, both in the atmosphere and in the ground, are treated. Again, these chapters provide a different pace to the general flow of material in the book.

Finally, the impact of trace combustion by-products on the environment and human health are examined in the context of risk analysis in Chapters 29 through 31.

Overall, this is a comprehensive reference book that should be useful to anyone interested in the emissions aspects of incineration. It is a handy compilation of different but complementary subjects related to the formation, measurements, and control of toxic combustion by-products in incinerators.

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Phosphorous Removal from Wastewater, Pollution Technology Review No. 189, R.P.G. Bowker and H.D. Stensel, editors. Noyes Data Corp., Park Ridge, N.J. 115 pages [ISBN No.: 0-8155-1250-3] U.S. List price: $45.00 (1990).

The book is a compilation of material from literature, demonstration projects, private communications, and a 1987 U.S. Environmental Protection Design Manual [*Design manual-Phosphorus Removal*, U.S. EPA, September 1987]. The book has been subjected to U.S. EPA peer review and has been approved for publication as an EPA document.

In Chapter 2, an overview of the steps employed in selecting a phosphorus removal strategy is presented. Design information and monitoring requirements are forwarded for both new and existing systems. An overview of the advantages and disadvantages of biological and chemical phosphorus removal alternatives is introduced. In subsequent chapters, these processes are discussed in greater detail.

Chapter 3 addresses the design, costing, and performance of biological phosphorus removal processes. The chapter is divided into three sections. In section one, phosphorus removal mechanisms are discussed. In the remaining sections, process descriptions and performance data are presented. The processes which are discussed in detail are the Phostrip process, the modified Bardenpho process, the A/O process, the University of Capetown (UCT) process, and the modified UCT process. When possible, full-scale design and performance data are presented. Factors affecting biological phosphorus removal are discussed in great detail along with cost and retrofit considerations. Three case studies are presented. A total of ninety-one citations are referenced.

Phosphorus removal by chemical addition is discussed in Chapter 4. The precipitation chemistry of aluminum and iron compounds with phosphate are discussed in detail. Several treatment trains are presented with possible application points. Chapter 4 also contains a lengthy table in which performance data for full-scale facilities

are presented. Equipment requirements for chemical handling and storage, dry chemical feeding and dissolution, dosage, control, and mixing and flocculation are discussed. Design methodologies for calculating chemical dosage and mixing and flocculation requirements as well as a fairly detailed design example are included in this chapter. Three case studies and some cost data are presented. Twenty-seven citations are referenced.

Sludge handling is introduced in the final chapter. Chemical and biological phosphorus removal processes are handled separately. For each type of sludge, characteristics and generation rates, gravity and flotation thickening, aerobic and anaerobic stabilization, sludge condition, several dewatering methods, incineration, and disposal options are discussed. Two case studies are presented and fifty-five citations are referenced.

In summary, *Phosphorus Removal from Wastewater* provides a good overview of the biological and chemical methods used to remove phosphorus from wastewater. The book has been sanctioned by the U.S. EPA and is recommended for designers and operators. The book would also make an excellent reference text for environmental engineering students.

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Controlling Volatile Organic Compound Emissions from Industrial Wastewater, Pollution Technology Review No. 197, Jeffrey Elliott and Sheryl Watkins editors. Noyes Data Corporation, Park Ridge, NJ., 363 pages [ISBN No.: 0-8155-1261-9], U.S. List Price $48.00 (1990).

Many chemical process plants have the potential to generate wastewater with high concentrations of organic compounds. Because the wastewater

collection and treatment systems are typically open to the atmosphere, emissions of volatile organic compounds (VOCs) are likely to occur.

This book examines VOC emissions and emission control technology for the wastewater from four different industries: the Organic Chemicals and Synthetic Fibers (OCPSF) industry; the Pesticide industry; the Pharmaceutical industry; and the Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) industry. The book also briefly examines the character of wastewater from the Pulp and Paper industry.

The text of this book was published from Industrial Wastewater Volatile Organic Compound Emissions - Background Information for BACT/LAER Determinations, prepared for the U.S. EPA in January, 1990. It contains six chapters, beginning with a brief introduction that describes the basis of the EPA document.

Chapter 2 describes the industries covered by the document. A combination of questionnaires, site visits, and sample collection was used to determine the general VOC-bearing character of wastewater from each of the industries.

Chapter 3 examines sources of air emissions from the wastewater collection and treatment operations used in the industries covered by the document. Operations range from drains and manholes to biological treatment basins.

VOC emission control equipment is discussed in Chapter 4. Control technology is discussed in three general categories: waste minimization, organic content reduction (prior to contact with air), and control of emissions during collection and treatment.

Chapters 5 and 6 focus on steam stripping as the technology favored by EPA for Best Available Control Technology/Lowest Achievable Emission Rate (BACT/LAER). Environmental impacts of steam stripping are discussed in Chapter 5. Chapter 6 presents an analysis of the costs of using steam stripping for wastewater emission control.

The Appendices, of which there are six, occupy more than half of the book's page count. Appendices A and B discuss emissions estimates and emission factors from wastewater collection and treatment operations. The emission factors estimate the emission of a VOC based on the influent concentration of the VOC, an approach that is fundamentally flawed for most well-mixed operations.

Appendices C and D present properties of VOCs and data on operation of selected steam strippers. Appendix E presents two draft EPA Reference Methods for determination of VOCs in wastewater. Appendix F provides an example facility analysis.

This book is important to those responsible for environmental compliance in the covered industries, if they have not already obtained the original EPA document. The book should not be considered a definitive description of the theory or practice of VOC emissions and emission control. Rather, it should be used as a technical reference regarding the likely regulatory position for the covered industries.

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Ground Water Modeling in Multilayer Aquifers: Steady Flow - Book 1, M.M. Aral, author/editor, Lewis Publishers Inc., Chelsea, Mi, 114 pages [ISBN No.: 0-87371-304-4] U.S. List Price: $90.00 (1990).

In this book M.M. Aral provides IBM-PC compatible applications software for analyzing quasi three-dimensional steady-state groundwater flow problems in confined, semi-confined, and unconfined multilayer aquifers. Detailed documentation of the underlying theory and Galerkin finite-element solution method are presented in the first three chapters. A user's manual is given in Chapter 4, and three case studies are described in Chapter 5.

The executable software provided with the text, SLAM. EXE (Steady Layered Aquifer Model), is written in Microsoft FORTRAN. It requires a 640K memory capacity and a low-density disk drive. For a 640K memory capacity, SLAM can simulate up to five aquifer layers with a six leaky confining layers (aquitards) using simplex triangular elements. The number of elements in each layer must be less than 950 and for a one-layer system, the number of nodes can not exceed 980. To provide conceptual flexibility, the numerical model can simulate up to 80 constant-head (Dirichlet), specified-flux (Neumann), head-dependent (Cauchy) boundary nodes in each layer. In addition, the model can simulate up to 30 wells in an aquifer layer. For higher memory environments, a special order may be placed with the author.

While the text is easy to read and understand, the reader is expected to have a working knowledge of basic concepts in hydrogeology to fully implement the numerical model. The user's manual is easy to use, and the author provides an automatic data generation feature that greatly reduces the task of input preparation.

The text provides a useful tool for preparing steady-state, multilayer-system analyses in a PC environment, and should be particularly useful for hydrogeologists, engineers, geologists, educators, and students.

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Point-of-Use/Entry Treatment of Drinking Water, Pollution Technology Review No. 188, U.S. Environmental Protection Agency and the American Water Works Association, Noyes Data Corporation, Park Ridge, NJ, 146 pages [ISBN No.: 0-8155-1249-X], U.S. List Price: $ 45.00 (1990).

Based on a conference on point-of-use treatment of drinking waters held in Cincinnati, Ohio, in June 1988, this book provides information of point-of-use and point-of-entry systems for treating drinking water. Until recently,

point-of-use systems were employed primarily to improve the aesthetic quality of drinking water by a municipal or private water supply. In recent years, however, these systems have also been employed for health reasons.

The book contains numerous sections written by 31 sets of authors. The book begins with an overview of point-of-use (POU) and point-of-entry (POE) systems. Topics discussed in the book include: POU/POE devices to meet drinking water standards, regulatory requirements for point-of-use systems; legal and practical considerations for control of POU devices; regulation of water treatment devices in California and Wisconsin (along with Federal Trade Commission regulations); product promotion guidelines/code-of-ethics; programs in the National Science Foundation relating to POU/POE systems; voluntary product validation; protocol for testing microbiological water purifiers; performance and applications of granular activated carbon, reverse osmosis, and ultraviolet light POU systems; precoat carbon filters; activated alumina for POU/POE removal of fluoride and arsenic; modeling studies; several case histories describing POU/POE applications; and various perspectives on POU/POE systems. The references cited in these various sections appear relevant and current (at the time of the writing of this book).

Although the book is more a compilation of proceeding papers, it does contain a fair amount of information on point-of-use/point-of-entry systems for treatment of drinking water supplies. The book should be useful for consulting engineers, environmental engineers, regulators, and residents of small communities.

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PCCHEMEQ: Prediction of the Flue Gas Compositions for Incinerator and Pyrolyzers

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Introduction

As a result in reduction in available waste disposal space throughout North America and Europe, serious considerations are being given to waste minimization, recovery of energy from waste and other disposal techniques. One of the alternative techniques is combustion of waste. This process produces waste gases which might require further treatment in order to satisfy environmental regulations. Chemical equilibrium codes have found applications in predicting the reaction products from combustion and pyrolysis processes.

Several software programs are available in the literature for the above applications [1,2]. Work done by Theodore and Reynolds [3] can assist you in the preliminary design and analysis of incinerators. Five different programs are available from Incinerator Consultants Inc. for calculating incinerator system parameters. The purpose of this review is to discuss a new software, PCCHEMEQ, available from T. C. International, 2533 Hazy Hollow, St. Antonio, TX 78255 (Telephone - (512) 698-0957).

PCCHEMEQ software is a software for predicting the flue gas compositions from incinerators and pyrolyzers. It is a thermal equilibrium program with calculations encompassing a large group of elements. The program can also perform the mass and energy balances for combustion, pyrolysis, gasification, rocket fuel burning, thermal cracking processes and slag/glass/soil melting.

The mathematical basis of the program is the thermal equilibrium program from NASA-Lewis [4]. This code is rated as the best for calculating equilibrium conditions in a variety of practical situations arising in combustion science. Calculation for equilibrium compositions can be based on equilibrium constant method or free energy minimization. The former has been used in PCCHEMEQ to develop compact, easy to debug and quick program. The program is written in BASIC language and can be run on a personal computer. A hard drive and a math coprocessor are recommended.

The nonlinear equilibrium equations are solved using an equilibrium constant method. The program can handle heterogeneous reactions. Twenty-three elements (0, C, N, H, Cl, F, Br, S, B, Si, Na, Mg, K, Ca, Al, Co, Cs, Pb, Ti, P, Fe, Cu, and electron) are included in the code. The database covers about 425 compounds including chlorinated dioxins and bipherryls (see Table I, compounds with asterisks are those that have equilibrium constant data which are included in equilibrium calculations).

The software comes with a manual [5]. It is divided into ten sections:

    (I) Introduction
    (II) Hardware and Software
    (III) Getting started
    (IV) Starting the Program
    (V) Exhibit 1
    (VI) Exhibit 2
    (VII) Exhibit 3
    (VII) Exhibit 4
    (IX) Exhibit 5
    (X) Appendix—A (Input screens)

The manual is very easy to follow. The

instructions given to run the program are not time consuming. Each exhibit section contains details on the problem solved, step by step input, computer screens and results.

To facilitate understanding of the software, the author has solved five problems which are discussed in the next section. It is our understanding that the program is being revised by the author to improve its capabilities. The manual has a few typographical errors.

Problems

1. Determine the products of combustion for an isothermal and isobaric conditions. The feed temperature is 25°C, feed pressure is 1 atm., reactor temperature is 1,000°C and volume of O_2 in oxidation is 21%. The input composition in g mole/min us given as: $O=10$, $N=37.62$, $C=2$, $H=2$, $Cl=1$, $F=1$, $Br=1$, and $S=1$.

2. Compute adiabatic flame temperature of natural gas (CH4) for the feed temperature of 25° C and feed pressure of 1 atm.

3. The equilibrium compositions at constant temperature and volume are calculated for the following operating conditions: reactor temperature = 1,000°C, volume = 1,000 liters and burn fuel (C_3H_8) with 10% excess air.

4. A flue gas stream is to be quenched from 330°C to 204.8°C. The feed composition in g mole/min is: $O_2=3315.6$, $N_2=25832.0$, $CO_2=3513.6$, $H_2O=4569.4$ and $SiO_2=69.3$. Compute the spray water rate.

5. A rotary kiln processes two waste streams: (a) 598.1 kg/hour of $Ca(OH)_2$ waste feed contaminated with 3.45% of emulsion fuel (by weight) and (b) 323.9 kg/hour of emulsion fuel. The kiln is operating at 600°C. Complete incinerator process takes place in a rotary kiln and a secondary chamber (after burner). #2 fuel oil is used as the supplemental fuel during the incineration. Compute required fuel fates for the incinerator process.

Experience

We found the computer program very interesting to run. Each of us was able to follow the instructions given in the manual. The program is user-friendly and easy to load. The program can be run using color or monochrome monitor. An IBM compatible personal computer with 480 RAM and or internal drive is required. The manual strongly recommends the use of a hard drive, printer, and a math coprocessor.

Environmental professionals involved in incinerator applications will find the program useful for their plants. The program can be easily used to train entry level engineers to solve incineration problems.

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4. Gordon, S., and McBride, B. J., Computer Program for Calculation of Chemical Equilibrium Compositions, Rocket Performance, Incidents and Reflected Shocks, and Chapman—Jouguet Detonations, NASA SP—273 (1976 revision), 1976.

5. PCCHEMEQ User's Manual, Rev. B., T. C. International, St. Antonio, TX 78255, pp.59, 1990.

Table I   LIST OF COMPOUNDS

1.*Al(c)	2.*Al(l)	3.*Al(g)	4.*AlCl(g)
5.*AlCl2(g)	6.*AlCl3(c)	7.*AlCl3(l)	8.*AlCl3(g)
9.*Al2O3(c)	10.*AlF(g)	11.*AlF2(g)	12.*AlF3(c)
13.*AlF3(g)	14.*Al6SI2O13(c)	15.*B(c)	16.*B(l)
17.*B(g)	18.*BHO2(c)	19.*BHO2(g)	20.*B2O3(c)
21.*B2O3(l)	22.*B2O3(g)	23.*B3H3O6(g)	24.*BrF(g)
25.*BrF3(g)	26.*Br2(g)	27.*C	28.*CCl4(g)
29.CCl4(l)	30.*CHCl3(g)	31.*CHCl3(l)	32.DICHLOROMETHANE(l)
33.*CH3Cl(g)	34.*CHO(g)	35.*CHNO(g)	36.*CH2O(g)
37.*CH4(g)	38.*CNCl(g)	39.NITROMETHANE(l)	40.*COCl(g)
41.*COCl2(g)	42.CBr4(g)	43.*C2H2(g)	44.C2HCl3(l)
45.11C2H4CL2(l)	46.C2H3Cl3(l)	47.*C2H4(g)	48.*C2N2(g)
49.*C3O2(g)	50.*CS(g)	51.*CO(g)	52.*CO2(g)
53.*COS(g)	54.*CS2(g)	55.*ETHYLENE OXIDE(g)	56.C2H6(g)
57.CH2Cl2(g)	58.C2Cl2(g)	59.C2CL4(g)	60.C2CL6(g)
61.CH3OH(l)	62.CH3OH(g)	63.*CH2O(g)	64.FORMIC ACID(l)
65.ACETIC ACID(l)	66.ACETONITRILE(l)	67.C2H5OH(g)	68.C2H5OH(l)
69.TRICHLOROETHYLENE(l)	70.TRICHLOROETHANE(l)	71.PROPANE(g)	72.PROPYLENE(g)
73.ACETONE(l)	74.PROPANOL(l)	75.PROPANOL(g)	76.N-BUTANE (l)
77.N-BUTANE(g)	78.N-BUTANOL(l)	79.ETHYL ACETATE(l)	80.DIETHYLAMINE(l)
81.N-PENTANE(l)	82.DIETHYLKETONE(l)	83.PYRIDINE(l)	84.BENZENE(l)
85.*Benzene(g)	86.BENZONITRILE(l)	87.BROMOBENZENE(l)	88.HEXANE(l)
89.1-HEXENE(l)	90.C6H5OH(l)	91.*Phenol(g)	92.ANILINE(l)
93.NITROBENZENE(l)	94.#1-FUELOIL	95.#2-FUELOIL(l)	96.#4-FUELOIL(l)
97.#6-FUEL-OIL(l)	98.N-HEPTANE(l)	99.TOLUENE(l)	100.*Toluene(g)
101.N-OCTANE(l)	102.ETHYLBENZENE(l)	103.O-XYLENE(l)	104.M-XYLENE(l)
105.P-XYLENE(l)	106.N-NONANE(l)	107.DECANE(l)	108.NAPHTHALENE(l)
109.UNDECANE(l)	110.1-DODECENE(l)	111.DODECANE(l)	112.1Cl-BIPHENYL
113.1242 AROCLOR(l)	114.1248 AROCLOR(l)	115.1254 AROCLOR(l)	116.1260 AROCLOR(l)
117.1Cl-BENZENE(l)	118.O-2Cl-BENZENE(l)	119.M-2CL-BENZENE(l)	120.P-2CL-BENZENE(l)
121.123-C6H3CL3(l)	122.4Cl-BENZENE(l)	123.5Cl-BENZENE(l)	124.6Cl-BENZENE(l)
125.*C6H5Cl(g)	126.*O-C6H4Cl2(g)	127.*M-C6H4Cl2(g)	128.*P-C6H4Cl2(g)
129.*123-C6H3CL3(g)	130.*C6Cl6(g)	131.*246-C6H2Cl3OH(g)	132.*Anthracene(g)
133.*Dibenzo-p-dioxin(g)	134.*1-Cl-p-dioxin(g)	135.*2-Cl-p-dioxin(g)	136.*2378-4Cl-p-dioxin(g)
137.*8Cl-p-dixion(g)	138.*Ca(c)	139.*Ca(l)	140.*Ca(g)
141.*CaCl(g)	142.*CaCl2(c)	143.*CaCl2(l)	144.*CaCl2(g)
145.*CaF(g)	146.*CaF2(c)	147.*CaF2(l)	148.*CaF2(g)
149.*CaO(c)	150.*CaO(g)	151.Ca(OH)2(c)	152.CaS(c)
153.CaCO3(c)	154.CaSO3.2H2O(c)	155.CaSO4(c)	156.CaSO4.2H2O(c)
157.*Cl2(g)	158.*Co(c)	159.*Co(l)	160.*Co(g)
161.*CoF2(c)	162.*CoF2(l)	163.*CoF2(g)	164.*Cs(c)
165.*Cs(l)	166.*Cs(g)	167.*CsCl(c)	168.*CsCl(l)
169.*CsCl(g)	170.*CsF(c)	171.*CsF(l)	172.*CsO(g)
173.*Cs2F2(g)	174.*Cs2O(g)	175.*Cu(c)	176.*Cu(l)
177.*Cu(g)	178.*CuCl(c)	179.*CuCl(l)	180.*CuCl(g)
181.*CuF(c)	182.*CuF(g)	183.CuCl2(c)	184.*CuO(c)
185.Cu2(g)	186.*CuO(g)	187.*CuF2(c)	188.*CuF2(l)
189.CuF2(g)	190.*Cu2O(c)	191.*Cu2O(l)	192.CuO.CuSO4(c)
193.*CuSO4(c)	194.*Cu3Cl3(g)	195.*F2(g)	196.*Fe(c)
197.*Fe(l)	198.*Fe(g)	199.*FeO(c)	200.*FeO(l)
201.*FeO(g)	202.*Fe2O3(c)	203.*Fe3O4(c)	204.Fe2(SO4)3(c)
205.*FeCl2(c)	206.*FeCl2(l)	207.*FeCl2(g)	208.*FeBr2(c)
209.*FeBr2(l)	210.*FeBr2(g)	211.*Fe2Br4(g)	212.*H2(g)
213.*HBr(g)	214.*HCl(g)	215.*HF(g)	216.*HCN(g)

Table I (continued)

217.*HO2(g)	218.*HN3(g)	219.*H2O(g)	220.H2O(1)
221.*H2S(g)	222.*K(c)	223.*K(1)	224.*K(g)
225.*KO(g)	226.*KBr(c)	227.*KBr(1)	228.*KBr(g)
229.*KF(c)	230.*KF(1)	231.*KF(g)	232.*KCl(c)
233.*KCl(1)	234.*KCl(g)	235.KNO3(c)	236.KClO3(c)
237.KCN(c)	238.*K2Br2(g)	239.*K2O(c)	240.KO2(c)
241.KOH(c)	242.*K2SiO3(1)	243.K2CO3(c)	244.*K2CO3(1)
245.KBrO4(c)	250.*K2SO4(1)		
249.KBrO4(c)	250.*K2SO4(1)	251.*K2SO4(g)	252.*Mg(c)
253.*Mg(1)	254.*Mg(g)	255.*MgO(c)	256.*MgO(1)
257.*MgO(g)	258.MgCO3(c)	259.Mg2Al4Si5O18(c)	260.*MgBr(g)
261.*MgBr2(c)	262.*MgBr2(1)	263.*MgBr2(g)	264.*MgCl(g)
265.*MgCl2(c)	266.*MgCl2(1)	267.*MgCl2(g)	268.*MgF(g)
269.*MgF2(c)	270.*MgF2(1)	271.*MgF2(g)	272.Mg2Cl4(g)
273.*MgS(c)	274.*MgS(g)	275.*Mg2Si(c)	276.*Mg2Si(1)
277.MgSO4.6H2O(c)	278.*MgSiO3(c)	279.*MgSiO3(1)	280.MgCL2.H2O(c)
281.*Mg2SiO4(c)	282.*Mg2SiO4(1)	283.Mg2TiO4(c)	284.Mg2F4(g)
285.*N2(g)	286.*NO(g)	287.*NO2(g)	288.*NH3(g)
289.*N2O(g)	290.*NOCl(g)	291.NH4F(c)	292.NH4Cl(c)
293.NH4OH(1)	294.NH4NO3(c)	295.*Na(c)	296.*Na(1)
297.*Na(g)	298.*NaCl(c)	299.*NaCl(1)	300.*NaCl(g)
301.*NaBr(c)	302.*NaBr(1)	303.*NaBr(g)	304.*NaF(c)
305.*NaF(1)	306.*NaF(g)	307.*NaO(g)	308.NaOH(c)
309.NaNO3(c)	310.NaNH2(c)	311.Na2CO3.H2O(c)	312.Na2O(c)
313.*Na2O(1)	314.NaN3(c)	315.Na2CO3.10H2O(c)	316.NaHCO3(c)
317.*Na2Cl2(g)	318.*Na2F2(g)	319.*Na2Br2(g)	320.Na2CO3(c)
321.*Na2CO3(1)	322.Na2SO3(c)	323.Na2SO4(c)	324.*Na2SO4(1)
325.NaN3(c)	326.*Na2SiO3(c)	327.*Na2SiO3(1)	328.Na3PO4(c)
329.*Na2Si2O5(c)	330.Na2Si2O5(1)	331.Na2S(c)	332.*O2(g)
333.*P(White;c)	334.*P(Red;c)	335.*P(g)	336.*P2(g)
337.*P4O10(g)	338.*PO2(g)	339.*PH3(g)	340.*PBr(g)
341.*PBr3(g)	342.*PSBr3(g)	343.*Pb(c)	344.*Pb(1)
345.*Pb(g)	346.*PbBr(g)	347.*PbBr2(c)	348.*PbBr2(1)
349.*PbBr2(g)	350.*PbCl2(c)	351.*PbCl2(1)	352.*PbCl2(g)
353.*PbF2(c)	354.*PbF2(1)	355.*PbF2(g)	356.*PbO(c)
357.*PbO(1)	358.*PbO(g)	359.*PbO2(c)	360.PbCO3(c)
361.PbC2O4(■=1)	362.*PbS(c)	363.*PbSiO3(c)	364.Pb2(g)
365.PbF4(C)	366.*Pb2SiO4(c)	367.*Pb3O4(c)	368.*S(c)
369.*SO2(g)	370.*SO3(g)	371.*S(1)	372.*S2(g)
373.*Si(c)	374.*Si(1)	375.*Si(g)	376.*SiO(g)
377.*SiO2(Quartz)	378.*SiO2(Low)	379.*SiO2(High)	380.*SiO2(1)
381.*SiO2(g)	382.*Ti(c)	383.*Ti(1)	384.*Ti(g)
385.*TiO2(c)	386.*TiO2(1)	387.*TiO2(g)	388.*Ti2O3(c)
389.*Ti2O3(1)	390.*Ti3O5(c)	391.*Ti3O5(1)	392.*Br(g)
393.*Cl(g)	394.*F(g)	395.*N(g)	396.*O(g)
397.*OH(g)	398.*H(g)	399.*ELECTRON	400.*H-(g)
401.*OH+(g)	402.*OH-(g)	403.*H2O+(g)	404.*O2-(g)
405.*O-(g)	406.*H+(g)	407.*Cl+(g)	408.*Cl-(g)
409.*Al+(g)	410.*C-(g)	411.*CO2-(g)	412.*F-(g)
413.*K+(g)	414.*KO-(g)	415.*Na+(g)	416.*NaO-(g)
417.*Mg+(g)	418.*NO+(g)	419.*Ti+(g)	420.C2H3Cl(g)
421.CH3CHO(g)	422.C3H3N(1)	423.C4H2O3(1)	424.13Butadiene(g)
425.C2H5COCH3(1)	426.Styrene(1)	427.C9H6N2O2(1)	

Destruction of Cyanides by Alkaline Hydrolysis in a Pipeline Reactor

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Free as well as organically-bound cyanides in a waste stream have been destroyed by alkaline hydrolysis in a simple pipeline reactor. This process has been running successfully at plant scale since 1969. Kinetic analysis shows that the hydrolysis is (pseudo) first order, but with two activation energies depending on temperature: 15.5 and 10.5 kcal/gm mole, for temperatures below and above 170°C, respectively. At lower temperatures (below 170°C), the rate limiting step is destruction of free and loosely bound cyanide, and at higher temperatures, the rate limitation is cyanide release from the more resistant organic entities.

Design of plant scale reactors, based on laboratory kinetic data, requires estimation of the extent of backmixing. This has been estimated successfully using literature reported values of axial diffusion coefficients for various geometries considered. Plant performance data have been found to correlate very close to the design estimates.

The pipeline hydrolysis reactor offers a novel and simple solution and should be applicable to cyanide disposal problems in a number of industries.

INTRODUCTION

The detoxification of cyanide-containing wastes has been and remains a major problem for segments of industry. Efforts are directed to cyanide removal on a continuing basis. Oxidation with chlorine and hypochlorite have been the most widely accepted method of cyanide treatment during the past 30 years, and is still the most common method since it can be carried out at ambient conditions. Other methods that use hydrogen peroxide, electro chemical oxidation, treatment with sulfur, UV/O_3 oxidation, wet air oxidation and biological oxidation are also in vogue to some extent [1–5].

Alkaline hydrolysis of cyanide, a reaction known since 1832 [6, 7], and studied as a possible ammonia synthesis in 1920 [8], has been reported as being useful for cyanide destruction in waste streams since 1972 [9–15]. Under alkaline conditions, the following reaction takes place in the temperature range 100° to 200–250°C:

$$R\text{-}CN + 2H_2O \rightarrow NH_3 + HCOO\text{-}R$$
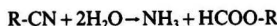
where R is a cation or loosely bound organic entity. Substan-

tially above 200°C, the formate decomposes to oxalate and carbonate, and at even higher temperatures the oxalate splits to carbon monoxide and hydrogen. Transition metal salts can catalyze the above mentioned reaction [14], although many metals and other complexing agents can slow the reaction considerably [10]. Although a commercial continuous reactor has been proposed [12], actual reported units appear to be operated in the batch (or swing-reactor) mode [10, 15], probably because of the substantial residence times required. Economically, hydrolysis competes very favorably with other cyanide destruction processes in terms of direct treatment cost, but is somewhat higher in capital outlay [2, 12].

We have had a continuous cyanide hydrolysis reactor in operation since January, 1969. The waste stream being processed emanates from a reaction using inorganic cyanide to manufacture DL-α-amino-α-vanillyl propionitrile, an intermediate ([16], compound II) in the production of L-methyldopa, an antihypertensive drug. Capital costs were kept low by the configuration of the reactor, which is a simple pipe. Laboratory kinetic data, reactor design considerations incorporating an axial dispersion model, and actual plant data are discussed in detail.
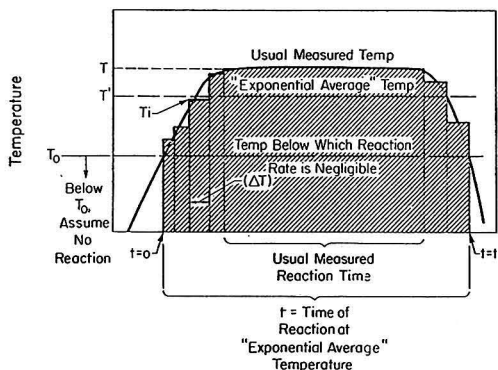
FIGURE 1. "Exponential Average" Temperature

FIGURE 2. Cyanide Concentration as a Function of Time

EXPERIMENTAL

Laboratory kinetic data were taken in closed tubes made of 316 stainless steel, each equipped with a thermocouple and pressure gauge and immersed in a hot oil bath, followed by quenching in water. At high temperature (short reaction time), it was necessary to take into account reaction occurring during heat-up and cool-down, and this was done by considering each experiment to have taken place at an "exponential average" temperature. This is defined for each experiment as the isothermal reaction temperature (instantaneous heatup) at which the actual measured cyanide concentration would have been achieved in the measured reaction time, t. Referring to Figure 1, and considering the reaction to have a linear arrhenius plot,

$$te^{-E/RT'} = \sum_{t=0}^{t} (\Delta t)e^{-E/RT}$$

where E = Activation Energy and R = gas constant. The "exponential average" temperature is thus:

$$T' = \cfrac{-E/R}{\ln \left[\cfrac{\displaystyle\sum_{t=0}^{t} (\Delta t)e^{-E/RT}}{t} \right]}$$

Failure to make this correction at high temperature for the cyanide hydrolysis (that is, assuming isothermal experiments) can result in errors in reported rate constants. Assuming the clocks were started at the moment of bath insertions, these would have been lower by 11 and 5%, respectively, for reaction temperatures of 270 and 230°C. Instead if the clocks were started at the moment of arrival at reaction temperature, reported rate constants for these same temperatures would have been higher by 8 and 2%, respectively.

Cyanide assays, during the laboratory kinetic studies, were carried out colorimetrically by contacting the sample with dichromate at pH greater than 12 for 15 minutes (dichromate removed interfering sulfite and sulfide moieties and hydrolyzed nitriles to free cyanide), acidification, and distillation of the resultant HCN into an alkaline scrubbing solution. Later, cyanide determinations were carried out using an Orion cyanide specific electrode. Specific ion electrode measurements were made at the same temperature as the calibration.

Radioactive tracer studies, carried out on the plant pipe reactor to measure axial diffusion (backmixing), used Bromine-82 in the form of aqueous KBr.
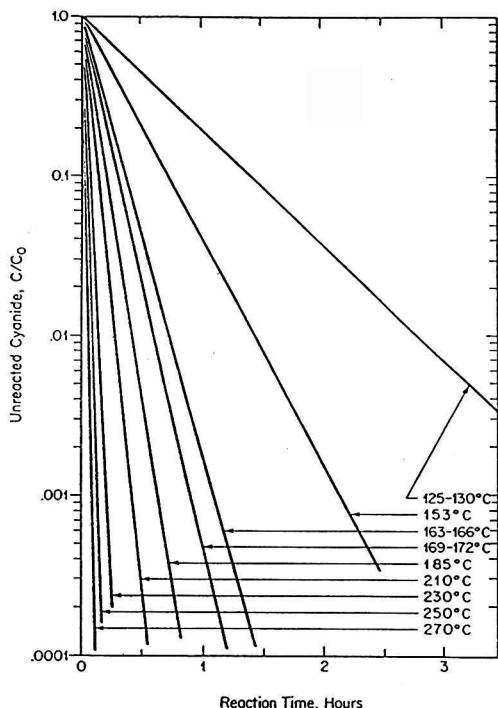
RESULTS AND DISCUSSION

a) Kinetic Data

The aminonitrile mother liquors being treated contained both free and organically bound cyanide, and the reduction in cyanide level in these hydrolysis experiments represents breakdown of both. Reduction in total cyanide from these liquors, as a function of time and temperature, is shown in Figure 2. Data points have been omitted for the sake of clarity. An Arrhenius plot drawn from these data (Figure 3) shows activation energy substantially reduced at temperatures above 170°C. To our knowledge, this is the first such report from a cyanide hydrolysis reaction, although analysis of the data of Wolfbeiss and Schindewolf [11], discussed in Section (d), shows a similar but smaller effect. We believe reduced activation energy for hydrolysis at higher temperatures (greater resistance to thermal effects) is caused by the presence of organically-bound cyanide. Reasoning for this is discussed in section (d). Table 1 compares the data from this work with those of others (all other studies used free cyanide). It is probably significant that best agreement of this work with the literature (lowest activation energy) is with that carried out over the highest temperature range (Wolfbeiss and Schindewolf).

b) Plant Reactor Design

Our first pipeline reactor for cyanide hydrolysis started operation in early 1969. It was designed conservatively with respect to axial dispersion, discussed below. After a number of years of experience, a higher capacity reactor was started up in 1973, designed with a higher degree of axial dispersion and suitable length compensation.

When designing a flow reactor with a very high conversion like the cyanide hydrolysis unit, it is important to avoid backmixing, which would, in this case, result in high levels of
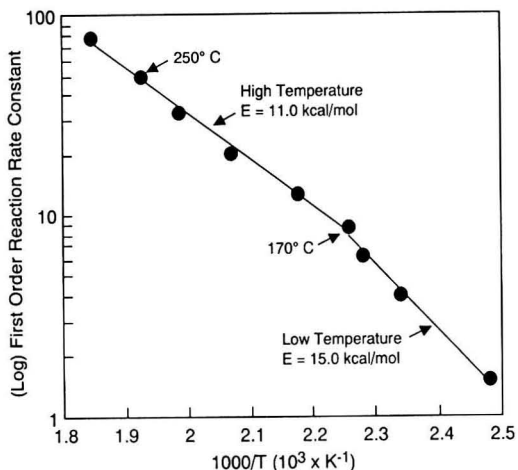
FIGURE 3. Cyanide Hydrolysis—Arrhenius Plot

FIGURE 4. Effect of Axial Dispension on Outlet Cyanide Concentration (Calculated)

$$\frac{dC}{dt} = D \frac{d^2C}{dX^2}$$

cyanide in the effluent. The axial dispersion model, originated by Danckwerts in 1953 [17], uses the analogy with molecular diffusion:

where C is concentration, t is time, X is length along the reactor, and D is an axial dispersion coefficient. It was later shown [18-20] that the residence time distribution (F or C curve) could be described by a reciprocal Peclet number, D/uL, where u is velocity and L is the reactor length. For a "closed" reactor, like the cyanide hydrolysis unit, the dispersion number D/uL can be related to the variance σ^2 on a measured residence time distribution by the relationship:

$$\sigma^2 = 2\frac{D}{uL} - 2\left(\frac{D}{uL}\right)^2 (1 - e^{uL/D})$$

During design of the expanded reactor (1973) with greater axial dispersion, computer programs developed by Rosas [21] were used to analyze the effect of pipeline geometry and reaction temperature. These programs numerically integrate F-curve data to evaluate conversion, and relate experimental F-curves to dispersion and CSTR cascade models. Figure 4 shows calculated cyanide destruction at 170°C as a function of residence time and dispersion number. A design procedure utilizing Figure 4, after estimating dispersion from data reported by Levenspiel [20], is shown in Table 2. As a result of that

Table 1 Comparison of Rate Constants and Activation Energies

Reference	Temp Range (°C)	(Pseudo) First Order Rate Constant (hr^{-1}) at 165°C	Activation Energy (Kcal/gm mole)
9. Kuhn and Rice	50–94	—	21.5
10. Okugawa	140–150	—	21.3
11. Wolfbeiss and Schindewolf	140–220	6.9	16.3
12. Hoerth, Schindewolf and Zbinden	100–190	10.4	20.1
13. Schindewolf	150–?	—	23.0
This work	130–170	—	15.0
This work	170–270	6.2	11.0

Table 2 Typical Reactor Design Procedure Based on Estimated Axial Dispersion

Reaction Conditions: Total Flow rate = 58.3 L/min (15.4 gal/min)
Temperature = 170°C
Input Cyanide Level = 2,500 mg/L
Required Effluent Cyanide Level: ≤5 mg/L

	Reactor Diameter (ID)		
	30.5 cm (12 inches)	45.7 cm (18 inches)	61.0 cm (24 inches)
1. Reynolds Number* $N_{Re} = \frac{d_t u \rho}{\mu}$	14,000	10,500	7,000
2. D/ud_t [from Levenspiel (20)]	0.4–0.5	0.4–0.6	0.5–0.9
3. Reactor Length, L (52 min. res. time)	41.1 m (135 ft)	18.3 m (60 ft)	10.4 m (34 ft)
4. Dispersion No., D/uL	0.0030–0.0037	0.010–0.015	0.029–0.053
5. Actual Residence Time for 5 ppm (From Figure 4)	54 min	56 min	58–64 min
6. Length Required for Actual Reactor	42.7 m (140 ft)	19.8 m (65 ft)	12.8 m [64 min] (42 ft)

*Based on actual fluid properties at 170°C.

Table 3 Typical Results of Radioactive Tracer Study (Plant Reactor)

Reactor Dimensions:	Length = 78.0 m (256 ft) Inside Diameter = 15.2 cm (6 inches) Volume = 1.40 m^3 (370 gallons)
Total Flow Rate:	43.4 L/min. (11.5 gal/min)*
Reactor Conditions:	Temperature 169°C Pressure 6.25 atm
F-Curve Results:	Mean Residence Time: 36.2 min Breakthrough Time: 27 min Variance σ^2: 0.0063 Dispersion No. (1/N$_{Pe}$), D/uL: 0.00315 Stirred Tank Equivalents: 159

*Including 12% additional volume from steam injection.

exercise, a 12-inch (30.5 cm) diameter reactor, 140 feet (42.7 m) long, was chosen as the ultimate design for the expanded reactor. The first reactor (1969) was designed on the same basis, but was so conservative that the deviation from plug flow was minimal and is shown by a typical measured F-curve in Table 3. Unfortunately, no tracer experiments were carried out on the larger (1973) reactor.

Corrosion data indicated that only two common materials of construction would stand up in extended service for the reactor: Teflon (all types) and Carpenter 20 alloy. The initial reactor was Teflon lined, but after several leakage problems in the initial unit, Carpenter 20 was used in the later one.

Economic considerations dictated use of steam injection for a reactor at 165–170°C. Energy requirements for electrical heating to higher temperatures, such as 250°C, made the option less attractive although at the shorter residence time (5.5 versus 45 minutes) would have created a capital saving. Ammonia was initially recovered from the reactor effluent, although one of the plants no longer finds this economical and has terminated the recovery operation.

After initial start-up, the plants using this process have reduced energy requirements to a very low level by judicious insertion of waste heat recovery units. On this basis, steam injection has been deleted from one unit in favor of a small trim shell and tube heat exchanger on the preheated feed stream. Condensate is also recovered. In the initial (1969) reactor, the design figure for cyanide in reactor effluent was 20 mg/L. This was reduced to 5 mg/L for the expanded (1973) reactor. Actual output from that reactor is 3–15 mg/L. Possible reasons for this excursion are discussed in section (d).

c) Plant Performance

Cyanide concentration and first order rate constant, as a

function of residence time in the 1969 reactor, is shown in Table 4. The test of different flow rates were carried out during start-up of that unit. It can be observed that with the exception of very extended residence times, the actual rate constants came out as predicted. Also, note the design figure of ca. 20 mg/L effluent (going to the plant waste treatment facility where enormous dilution takes place) was attained at the design residence time of 40–50 minutes.

No such data are available for the expanded unit (1973 reactor design), which is in operation at two facilities. Average performance of these units, however, is a conversion of 50.8 L/min feed (12 gal/min plus steam injection) containing 2000 to 3000 mg/L total cyanide to 3–15 mg/L. Occasionally, reactor effluent rises briefly to 25–30 mg/L. Possible reasons for difficulty in consistently attaining the 5 mg/L design figure are discussed in section (d).

d) Organic Cyanides and Reduced Activation Energy

As indicated, hydrolysis of the cyanide entities in these real plant streams has shown anomalous behavior, by exhibiting multiple activation energies. This behavior can probably be explained by the presence of free and bound cyanide entities, or that of bound entities of varying resistance to hydrolysis.

Table 5 compares reaction rate constants and activation energies at low and high temperatures (130–150°C and 170–180°C, respectively), for this work and that of Wolfbeiss and Schindewolf [11]. (Note: The activation energy of 10.5 Kcal/gm mole in this work is valid up to 270°C). In the 130–150°C range, both reaction rate constants and activation energies for the two works are in reasonable agreement. The 170–180°C data, however, show 30–50% higher reaction rates and a 50% higher activation energy in Wolfbeiss and Schindewolf.

Since the clear difference between this work and Wolfbeiss and Schindewolf is the presence, in ours, of a number of organically-bound cyanide entities, it is reasonable to conclude that at lower temperatures, the rate limiting step in our work is destruction of free and loosely bound cyanide, and resultant agreement with the work of others on exclusively inorganic material. At higher temperatures, rate limitation in our work is presumably cyanide release from the more resistant organic entities, which do not respond as quickly as inorganics to increased thermal stress.

A mixed population of varying resistances to hydrolysis could also explain the inability of the plant reactor to consistently attain very low cyanide levels (5 mg/L: $C/C_0 = 0.002$). It is conceivable, even probable, that a highly resistant cyanide entity might exist in the 3 to 30 mg/L range. In the laboratory, cyanide analyses at low levels (≤ 5 mg/L) were difficult to measure with precision. It is possible that another mechanism

Table 4 Plant Reactor Performance Actual Versus Expected Rate Constants

Reactor Dimensions: Refer to Table 3

Total Flow Rate* (L/min)	Mean Residence Time (min)	Reactor Conditions		Total Cyanide Conc (mg/L)		(Pseudo) First Order Rate Constant, k (hr^{-1})	
		Temp (°C)	Pressure (Atm)	Inlet	Outlet	Actual	Expected
28.4	50	169	6.2	1857	19.6	5.46	7.7
31.8	44	169	6.2	1821	17.5	6.33	7.7
35.2	40	170	6.2	1893	20	6.82	7.7
37.1	38	165	6.2	1821	34.2	6.28	6.5
38.5	37	165	6.2	1728	30	6.57	6.5
42.3	33	165	6.2	1893	33.4	7.34	6.5
46.0	30	165	6.2	1875	34.1	8.01	6.5
46.0	30	170	6.2	2214	34	8.35	7.7

*Including 12% additional volume from steam injection.

Table 5 Reaction Rate Constants and Activation Energy as a Function of Temperature: This Work Versus Wolfbeiss & Schindewolf [11]

Temperature	Reaction Rate Constants $[(hr)^{-1}]$	
	This Work	Wolfbeiss & Schindewolf
130°C	1.5	—
140°C	—	2.2
150°C	3.1	3.5
170°C	8.5	11.0
180°C	11.0	16.2
	Activation Energy (Kcal/gm mol)	
(130–150°C)	15.5	17.3
(170–180°C)	10.5	15.7

change at that level, reflective of a yet more resistant entity, might have been masked by assay difficulty. By the time of the new 5 mg/L specification in the factory reactor in 1973, considerably better analysis was available.

It *is* possible, although not probable, that axial dispersion in the 1973 reactor could have contributed to the difficulty in obtaining the 5 mg/L level with consistency. Table 6 shows the unlikely axial dispersion numbers (from Figure 4) which would be required to raise cyanide levels in the effluent to those exhibited in the reactor (3–15 mg/L, occasional peaks to 25–30 mg/L), with no decrease in reaction rate constant. Thus, we conclude the presence of more resistant bound cyanide species.

Table 6 Dispersion Numbers Required in the Reactor (Table 2) to Cause Observed Cyanide Level in Plant Reactor Effluent

Dispersion Number (D/UL)	Cyanide in Effluent* (mg/L)
0 (plug flow)	1.5
0.0036 (expected)	2
0.017	3
0.027	4
0.045	6
0.096	12
Laminar	20

*From Figure 4 • Actual Plant Effluent = 3–15 mg/L

CONCLUSIONS

Alkaline hydrolysis of the cyanide waste stream has been a reliable and successful installation. Use of a simple pipeline reactor configuration has permitted significant savings of capital without any economic and performance penalty. It should be possible to use this technology for some of the difficult cyanide removal problems in other industries. Use of existing correlations to quantify backmixing allows easy design of large-scale cyanide destruction reactors based on laboratory kinetic data.

ACKNOWLEDGMENTS

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Extraction and Recovery of Lead Species from Soil

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The remediation of lead contaminated soil at Superfund sites and urban soil is a serious concern, given the grave effects of lead exposure and the pervasive nature of the threat. The lead species of interest are elemental lead, lead sulfate, basic carbonate of lead and lead dioxide. This paper describes work done to solubilize these species and recover the contaminants as salable lead sulfate. Proof of concept was done using the pure chemicals. After this, bench scale experiments were done using a soil that was dosed with varying amounts of the contaminants (total lead from 1,000 to 10,000 ppm) and better than 80% of the contaminants was recovered as lead sulfate. The treated soil passed the TCLP test with 3.0 ppm lead, showing that it could be be redeposited on site. A pilot-plant scale-up is being explored.

INTRODUCTION

Of the more than 1200 Superfund sites on the National Priority List (NPL), roughly a third have lead as an identified contaminant, and of these about half have a documented release of lead to air, surface water or ground water. In addition, there are several RCRA corrective action sites with lead as a contaminant. Furthermore, lead is a problem in several other hazardous sites. Lead contamination in urban soil (including lead from paint associated with demolished old houses) is a serious threat. The adverse health effects due to lead exposure, even at low levels, are well documented [2–6]. Allowed lead concentrations in drinking water have continuously been lowered, as were also the blood lead levels in children requiring medical attention. Given the ubiquitous nature of the contaminant and the pervasive and insidious adverse effects of exposure, it is not surprising that the problem has received national attention. The remediation of lead contaminated soil should be a prime concern since from the soil the contamination may spread to other media. It is heartening to note that the use of lead-free gasoline has really resulted in environmentally beneficial results. About 20 years ago, it was shown that lead concentrations in Greenland ice and snow had risen 200-fold since ancient times [1], this increase being attributable mainly to the use of leaded gasoline. Partly due to this evidence, the U.S. and other countries began restricting the use of lead additives in gasoline. In the United States, the consumption of lead additives fell by more than 90% between 1970 and present [6]. It has been found that the lead concentration in Greenland snow have decreased by a factor of 7.5 during this twenty year period. This large decrease in the pollution of the global troposphere by lead is testimony to the effect of environmental measures taken and should act as an incentive to vigorously pursue the remediation of lead contaminated soil. The Records of Decision (RODs) signed for a number of metal contaminated NPL sites prescribe either excavation and off-site disposal, solidification and stabilization or capping. These measures are palliative in nature and entail depletion of precious natural resources (the metals). The metals originally have
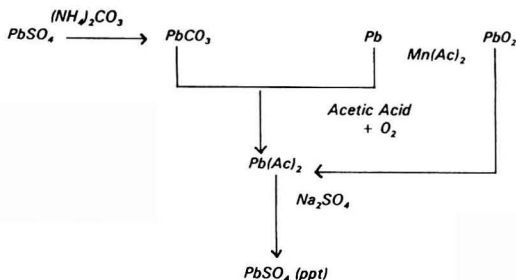
FIGURE 1. Lead solubilization chemistry.

been mined out and treated at considerable cost and to consign them to the grave, without the hope of resurrection, does not make economic sense.

There is a need to develop innovative technologies that will efficiently remove the toxic metals from the soil, using processes that are environmentally acceptable (no adverse releases to the media) and to recover the metals in some usable form. This paper describes an effort to address this need identified above, as related to lead. The contaminants of concern are metallic lead, lead sulfate, lead carbonate and lead dioxide. These are insoluble in water and hence have to be solubilized to get them in an aqueous solution. The lead then has to be precipitated and recovered as, say, lead sulfate, a marketably commodity. The reagents used should be safe to handle and they should be environmentally acceptable. These were the objectives and constraints of this piece of work. Some work has been done by the U.S. Bureau of Mines (BOM) on the remediation of lead contaminated soil at battery breaker sites [7]. Nitric acid was used for leaching. This has the disadvantage of possible release of toxic oxides of nitrogen. BOM also tried fluosilicic acid and subsequent electrowinning of lead. The great drawback in the nitric acid process was that it required about 70-97 hours for the three-step process.

In the present work, it was first demonstrated that the lead contaminants of concern could be solubilized in a three step process (Figure 1) and then recovered by precipitation as lead sulfate. The first carbonation step converts the lead sulfate into the carbonate. The second step uses acetic acid and oxygen, thereby converting the lead carbonate to lead acetate and also oxidizing elemental lead to lead acetate. The third step uses manganese acetate to convert lead dioxide into lead acetate. In this initial proof-of-concept stage using the lead species, about 90% of the lead compounds were solubilized and recovered. The process required about six hours, if lead dioxide was present; otherwise, it took only 90 minutes. The three-step process was then applied to a soil that was dosed with the lead species in question in concentrations ranging from 1,000 to 10,000 ppm of total lead. More than 80% of the lead in the soil was extracted and recovered as lead sulfate. The treated

soil passed the Toxicity Characteristic Leaching Procedure (TCLP) test, the TCLP extract giving a lead concentration of 3.0 ppm. Thus the soil is suitable for redeposition at the site.

MATERIALS AND METHODS

Materials

The characteristics of the chemicals used are set forth below:

Elemental lead: Powder 99.5% Johnson Mathey
Lead Shot: Johnson Mathey
Diam. 0.09"
Lead granules with the following Particle size distribution:

Mesh Size	Weight %
+30	24.5
−30−+50	65.2
−50−+100	9.4
−100	0.85
Lead dioxide (99.5%)	Aldrich
Manganese acetate	Spectrum

Soil

A sample of Louisiana soil was spiked with the lead species of concern to give total lead concentrations of 10,000, 5,000, and 1,000 mg/kg. The Louisiana soil had the following characteristics:

Particle size distribution (wt %)

Table 2 Elemental Lead Dissolution in Oxygenated Acetic Acid (Lead Added, 10,000 ppm; Oxygen Flow, 60 mL/min.)

Time (min.)	Conc. of acid	Lead in soln. ppm	pH Initial	pH Final
10	1.0 M	7,200	2.37	3.22
20	1.0 M	8,910	3.22	3.19
30	1.0 M	9,090	3.19	3.24
40	1.0 M	9,230	3.24	3.25
50	1.0 M	9,370	3.25	3.26
60	1.0 M	9,550	3.26	3.29
70	1.0 M	9,550	3.29	3.28
10	0.1 M	7,330	2.89	4.09
20	0.1 M	7,470	4.09	4.15
30	0.1 M	7,510	4.15	4.16
40	0.1 M	7,960	4.16	4.20
50	0.1 M	8,050	4.20	4.20
60	0.1 M	8,020	4.20	4.20
70	0.1 M	8,020	4.20	4.20

Table 1 Lead Sulfate (Equivalent 10,000 mg Pb/L Solubilization With Ammonium Carbonate & Acetic Acid (5 Min.)

Amm. carbonate to PB ratio	Acid Molarity	Lead in Soln. mg/kg	%
2.13	0.13	8,201	82
2.13	0.13	7,959	79.6
2.13	1.0	8,713	87.1
2.13	1.0	8,982	89.8
3.20	1.0	8,982	89.8
3.20	1.0	9,368	93.7

Table 3 Lead Dioxide Conversion to Lead Acetate by Manganese Acetate (One Hour Reaction Time)

Run No.	Mn acetate g/500 mL	Lead dioxide Equivalent Pb	Lead in solution ppm	%
1	0.5	2000 ppm	654	33
2	0.5	2000 ppm	654	33
1	1.0	2000 ppm	1164	58
2	1.0	2000 ppm	1205	60
1	1.5	2000 ppm	1057	53
2	1.5	2000 ppm	1019	51
1	2.0	2000 ppm	961	48
2	2.0	2000 ppm	1033	52

Particle Size	Value	Unit
Sand	1.0	%
Silt	89.0	%
Clay	10.0	%
Cation Exch. Cap	10.1	meq/100q
Moisture	22.0	%
Soil pH	4.5	%
Tot. Org. C.	0.42	

Methods

Stirring the reaction mixture was initially done by using a Waring blender; subsequently, this was accomplished by using a Lab Master Mixer with R-100 impeller attached (High shear, non-dispersing impeller).

Analysis

Lead analyses were done by AA Spectrometry.

EXPERIMENTAL

Typical procedures for the solubilization of individual lead species are given below:
1. Conversion of lead sulfate to the carbonate with ammonium carbonate and dissolution of the carbonate in acetic acid.

    A solution of ammonium carbonate (500 ml; conc. 9.87 g/l) was placed in a Waring blender and lead sulfate (7.47 g) was added to the solution. A blender speed of 14 was maintained for 5 minutes. The slurry was filtered and the precipitate was treated with 500 ml of acetic acid (1.0 M) and stirred for ten minutes. After filtration, three samples of the clear solution were withdrawn and analyzed for lead. The experiment was repeated, changing only the concentration of ammonium carbonate solution from 9.87 to 14.63 g/l.

    The results are presented in Table 1.
2. Solubilization of Elemental Lead in Oxygenated Acetic Acid Lead powder (5.0 g) was added to 500 ml of 1.0 M acetic acid in a beaker. Oxygen was passed (60 ml/min.) while maintaining vigorous agitation. Sample aliquots were withdrawn every ten minutes, for a period of 70 minutes and the samples were analyzed for lead. The experiment was repeated, using 0.1 M acetic acid.

Table 4 Rate of Conversion of Lead Dioxide (0.5776 g in 2.0 L of 1.0 M Acetic Acid) to the Acetate by Manganese Acetate (6.0 g; Temperature: 22–23 C)

Time (min.)	Lead in solution (ppm)
0	0
20	6.71
40	75.50
60	124.30
80	158.50
100	187.40
120	191.60
140	253.25
160	246.00
180	229.00
200	248.75
220	286.75

percent conversion 91

The results are presented in Table 2. To study the influence of lead particle size on the rate of dissolution in oxygenated acetic acid, the experiment was repeated using lead shot (0.90″) and lead granules.
3. Conversion of Lead Dioxide into Lead Acetate using Manganese Acetate. Lead dioxide (1.15 g) and manganese acetate (0.5 g) were added to 500 ml of 1.0 M acetic acid in a beaker. The contents were agitated for one hour using a paddle mixer. Three samples were taken and analyzed for lead. The amounts of manganese acetate added were changed in subsequent runs. The results are presented in Table 3. As only about 50% conversion was achieved in the above 1-hour reaction time, a second set of experiments was done, for four hours. Here the rate of the reaction at room temperature was studied. In order to achieve the abrasion that would occur with real soil, the reaction was conducted in the presence of added sand. A typical run was as follows:

    A mixture of lead dioxide (0.5771 g), manganese acetate (4.0 g) and clean sand (250 g) was added to 2000 ml of 1.0 M acetic acid in a 4 L beaker. The mixture was kept stirred (1000 RPM) for 4 hours. Periodically, samples were collected via a fractional collector fitted with an on-line filter. The rate of solution withdrawal was 1.025 mL/min, and a total of 20.5 mL of solution was collected per collection tube. The temperature of the slurry was 21–23°C. The results are presented in Table 4. Extraction of soil spiked with various levels of

Table 5 Lead Removal Efficiency From Contaminate Soil (250 g; Total pB = 10,000 MG/KG; Soil/Soln. Ratio 1:8)

Step No.	Reagent	Lead (ppm) in filtrate	Filtrate Vol. (mL)	% Pb removed
I	Amm. carbonate	5.401	1860	0.375
II	Oxygen + acetic acid	847.262	1866	65.07
	Wear washing	207.268	440	3.65
III	Mn. acetate	183.215	1880	13.78
SUB TOTAL				82.88
REPETITION OF THE 3-STEP EXTRACTION ON RESIDUE FROM ABOVE				
I	Amm. carbonate	0.776	1980	0.0165
II	Oxygen + acetic acid	62.598	1820	4.5557
	Washing	32.774	545	0.714
III	Mn. acetate	12.225	1910	0.934
	Washing	5.202	495	0.103
SUB TOTAL				6.370
TOTAL				89.25

Table 6 Lead Removal Efficiency from Contaminated Soil (250 g; Total Pb = 5,000 mg/kg; Soil/Soln. Ratio 1:8)

Step	Reagent	Lead (ppm) in filtrate	Filtrate vol. (mL)	% Pb removed
I	Amm. carbonate	5.545	1850	0.6883
II	Oxygen + acetic	428.55	1860	63.77
	Washing	94.373	465	3.51
III	Mn. acetate	96.623	1840	14.21
	TOTAL			82.18

lead species with total lead of 10000, 5000, and 1000 mg/kg.

The foregoing experiments showed that the chemistry of the three stage conversion of the lead contaminants to soluble lead acetate is workable and sound. The next stage was to apply these principles to a clean soil that was spiked with these contaminants. Clean Louisiana soil that has been characterized as described previously, was spiked with the contaminants and the following three-step process was carried out:

Step I. Treatment of soil with ammonium carbonate solution for 30 minutes and filtration.
Step IIa. Addition of acetic acid and oxygen and filtration.
Step IIb. Washing the residue from filtration of above, with water.
Step III. Addition of manganese acetate and acetic acid followed by filtration.

The following was a typical procedure:
Louisiana soil (250 g) was spiked with a mixture of the following lead species (total Pb = 10,000 mg/kg):

Lead sulfate	60%
White lead	20%
Elemental lead	10%
Lead dioxide	10%

This spiked soil was taken through the three step process and the lead recovered in each step was determined. A soil to solution ratio of 1:8 was used in steps I, IIa and III while in the water washing step IIb, a soil solution ratio of 1:2 was used. The experiment was repeated with soil contaminated with total lead of 5,000 and 1,000 mg/kg. The results are presented in Tables 5, 6, and 7.
Recovery of lead from the filtrate from above.

The filtrate from the above extraction process was treated with sodium sulfate to precipitate and recover the lead (Ratio of Sodium sulfate/Pb was 4.2) 99.8% of the lead in solution was recovered as lead sulfate. A Toxicity Characteristic Leaching Procedure (TCLP) was done on the treated soil.

RESULTS AND DISCUSSION

The results are presented in Tables 1 thru 7. The conversion of lead sulfate to the carbonate and subsequent dissolution in acetic acid (Table 1) proceeded smoothly and rapidly. Conversion was achieved in 5.0 minutes. This rapid rate of conversion is attributable to the large difference in the values of the solubility products of the two compounds:

Lead carbonate, $Ksp = 3.8 \times 10^{-14}$ (18°C)
Lead sulfate, $Ksp = 1.06 \times 10^{-8}$ (18°C)

Lead sulfate is the principal contaminant at lead battery sites and solubilization of it will constitute an important step in soil remediation. Vigorous agitation is necessary so that no protective coating of the carbonate on the sulfate is formed. Other reagents for solubilizing the lead sulfate were tried. Ammonium acetate did solubilize lead sulfate, to a limited extent. The dissolution of elemental lead in oxygenated acetic acid was studied under different conditions such as concentration of acid, oxygen flow rate, time of reaction and lead particle size. Better than 95% of lead was solubilized in about one hour. The redox potential for this reaction was calculated to be about +1.3 volts. This positive value indicated the feasibility of the reaction. Table 2 shows the results with lead powder. As lead goes into solution, an acetate buffer is formed in which the concentration of acetate increases gradually. This is reflected in the gradual increase in pH. Under conditions identical to those used with lead powder, only about 25% of the lead shot went into solution and about 65% went into solution when granulated lead was used. This shows that the particle size of elemental lead in the soil will determine the time required to solubilize lead.

Lead dioxide is a refractory substance. The solubilization of this compound was tried using a variety of reagents. Tables 3 and 4 give the results obtained with manganese acetate. Only about 50% conversion to acetate was obtained in one hour. 91% conversion was achieved by extending the time to four hours. Other reagents tried, with less successful results were manganese chloride, oxalic acid, and ammonium bisulfite.

Tables 5 thru 7 give the results of extracting the lead species from a soil spiked with various levels of lead. About 80 to 89% of the lead species was recovered as lead sulfate. The treated soil passed the TCLP test, with the leachate showing 3.0 ppm lead. A passing grade in this test is 5.0 ppm. The good recovery of the contaminants coupled with the fact that the treated soil passed the TCLP test constitute the best recommendation for the process. Plans for a pilot plant scale-up are under way.

The laboratory and bench-scale experiments described above indicate the great promise of the process envisaged. There are several advantages associated with the process. Chief among them are: a) environmental acceptability, b) short process time (about 6 hours if lead dioxide is present as a contaminant, otherwise only 1.5 hours), c) good recovery of lead sulfate,

Table 7 Lead Removal Efficiency from Contaminated Soil (250 g; Total Pb = 1,000 mg/kg; Soil/Soln. Ratio 1:8)

Step No.	Reagent	Pb (ppm) in filtrate	Filtrate vol. (mL)	% Pb Recovered
I	Amm. carbonate	2.583	1800	1.860
II	Oxygen + acetic	75.347	1910	57.56
	Washing	24.116	450	4.36
III	Mn. acetate	21.316	1865	15.90
	TOTAL			79.68

and d) treated soil that passes the TCLP test, thus rendering it fit for redeposition on site. It should however be pointed out that the contaminated soil used here has not been subjected to weathering. The treatment by this process of a Superfund weathered soil may require more stringent/altered conditions.

While elemental lead, lead sulfate, lead carbonate and lead dioxide are the usually encountered contaminants, it would be advisable to use x-Ray diffraction analysis to identify the species actually encountered in a particular soil, and then design suitable alterations to the remediation process.

The method described here may be suitable for remediating lead-contaminated urban soil. The lead species are almost the same. The process may be applicable to treating lead paint chips. Here, we may have lead in the form of naphthenate, requiring some modified treatment. No serious impediments to the extension of this process to the treatment of urban-lead-contaminated soil and lead paint chips are seen. Work on these topics is being initiated.

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DISCLAIMER

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Plant Experience Using Hydrogen Peroxide for Enhanced Fat Flotation and BOD Removal

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Hydrogen peroxide (H_2O_2), is known in the food processing industry to reduce COD, BOD, to prevent anaerobic conditions in pipes, tanks and lagoons and to remove malodorous sulfides in effluents from anaerobic wastewater treatment. It has recently been shown to also provide effective solids removal from food processing wastewater. The wastewater of food processing plants often contains a very high loading of organic material consisting of fat, oil and grease (FOG), resulting in unacceptable BOD and COD levels. Since many wastewater treatment systems are being pushed to the limit of their capacity or are already overloaded, the high FOG loading cannot be removed well by the conventional means of treating the wastewater with dissolved air flotation or grease traps. As a result, many food processors are paying surcharges for not being in compliance with the tight discharge limits. To overcome these problems, a process has been developed using H_2O_2 for enhanced FOG recovery and BOD removal. The process is based on the formation of microbubbles which attach themselves to the FOG particles and float them to the surface where they can be easily skimmed off. In addition to meeting effluent standards, the process has been able to yield a material that is very renderable and suitable for reuse. Technical and operational data of several industrial applications in the U.S. and Canada are presented, together with process costs. H_2O_2 treatment will generally be most applicable when improvement of solids removal is required without major investment costs, e.g. emergency situations, during seasonal peaks or increased production.

INTRODUCTION

Like other industries, the food industry has to face increasingly tighter regulations for meeting environmental concerns [1]. This results in a dramatic build-up of costs associated with processing by meeting the water discharge permits. In order to comply with these permits, food processors are confronted with heavy capital expenditures or, when not in compliance, with significant surcharges. Fats, grease, and oil are significant components of food processing plant wastewaters which cause severe environmental problems. Efforts are continuing to develop new process technologies which reduce water consumption or organic load. For example, the poultry industry has succeeded in reducing the amount of water consumed per bird processed from 9-10 gallons per bird to as low as 3.5 gallons within a few years [2].

In addition to reducing water consumption, plant operators have made increasing use of chemicals and processes that have been utilized on a large scale in wastewater treatment facilities from other industries, e.g. municipal wastewater treatment facilities which are now tailored to the specific needs of individual food processing plants. One chemical, that has been widely used for many years in wastewater treatment is hydrogen peroxide. Its unique properties as a strong oxidizer, its good germicidal properties and its simple use as a liquid source of oxygen have made hydrogen peroxide the chemical of choice for the purification of polluted wastewater streams [3-10]. An added benefit, especially for applications in the food industry, is the fact that H_2O_2 does not bring any additional salts or compounds to the water system. Any residual H_2O_2 left over will decompose to pure oxygen and water. The application of H_2O_2 in cleaning food processing wastewater containing fat, oil and grease will be detailed in the following chapters.

REMOVAL OF FOG FROM WASTE WATER

Demulsifying Techniques

Since most discharges contain free fat and grease in suspension as well as emulsified material, it might be necessary to break down the emulsion prior to the flotation step in order to get efficient separation. One of the most commonly applied techniques for demulsification takes advantage of the fact that many emulsions are less stable at low pH conditions. It has been demonstrated that oil droplets have a negative charge at high pH values [11]. By the addition of acid, this charge is neutralized and coalescence of the oil droplet may then occur. The process is relatively simple and can be automatically controlled to an empirically determined optimum pH which helps in maintaining treatment efficiency. Acidification and charge neutralization are very useful as a primary demulsification stage where the oil concentrations are relatively high and when the recovery product is considered for reuse. Polyvalent cations such as Fe^{3+} or Al^{3+} can also be used to destabilize emulsions not only by charge neutralization, but also through hydrolysis by providing bridges across which emulsified droplets can be linked.

The polyvalent cations also provide additional benefits by presenting surfaces onto which physical adsorption can occur and, in the process of hydrolysis, by entraining oil and grease materials within the floc structure. One disadvantage in using Fe^{3+} or Al^{3+} cations is that the recovered material is inevitably contaminated with the metal hydroxide which makes the product unsuitable for reuse or at least lowers its reuse value. Apart from the disadvantage imposed by use of metal cations for breaking emulsions in reducing the quality of the recovered material these reagents also generate metal hydroxide sludges that have to be disposed of. In both of these aspects water-soluble organic polyelectrolytes have significant advantages in that the concentrations needed are only a few milligrams per liter and that they do not generate extra quantities of waste for disposal. Polyelectrolytes act as demulsifiers either as coagulants (destabilization via charge neutralization) or flocculants (by providing interparticle bridging). Cationic polymers have been proven to be very effective in the treatment of oily emulsions [13]. The negative charge present in an emulsified oil droplet explains the fact that anionic and non-ionic polyelectrolyte are relatively poor for such systems. Among the cationic polyelectrolytes available commercially are polyquarternary salts (e.g. PDADMA) and polyamines. Charge density is controlled by copolymerization with non-ionic acrylamide.

Separation Techniques

Simple flotation of the lighter fat particles occurs in so-called grease traps, where the flow enters a chamber (typically with 20–60 minutes retention time) at the top, then flows downward under a baffle near the exit, preferably with inlet and outlet weirs to distribute the flow evenly. The oil, fat, and grease are given time to collect on the inlet side of the baffle, and are removed periodically by skimmers.

The installation of a grease trap only results in a partial recovery of oil and grease and may be adequate when the flow only represents a small share of the total (oil and grease free) discharge.

Flotation can be substantially improved by the introduction of air into the flotation chamber in the form of very fine bubbles. The bubbles attach themselves to the FOG particles and raise them quickly to the surface where they can be removed by skimming. The size of the air bubbles is very important. Studies have shown that the fat particles first nucleate with microbubbles generated from dissolved gases; these microbubbles then act as bridges for the formation of larger bubbles. The important point is that the rate-limiting step is the velocity of the formation of a microbubble or its attachment onto the particle surface [12]. Once the bubbles have attached themselves to the particles the bubbles rise. First they form a lattice which appears like a loose sponge, then the bubbles tighten into a froth. This tightening process results in the squeezing out of a great part of the occluded water.

In so-called dissolved air flotation, influent or recycled effluent is saturated with air to a pressure of 3–6 bars and then released at atmospheric pressure into the rising waste water stream with formation of air bubbles that are initially 50–100 μm in diameter. Fig. 1 illustrates a typical dissolved air flotation system.

Improved Grease Trap and D.A.F. Cell Performance by H_2O_2 Addition

In the presence of metals and organic material such as blood, grease or meat particles, hydrogen peroxide gradually decomposes in waste water according to the following equation:

$$2\ H_2O_2 \rightarrow 2H_2O + O_2$$
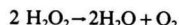
When applied correctly this effect will form oxygen microbubbles which are significantly smaller in diameter than bubbles typically released from water oversaturated with air. Since the number and the size of the air bubbles determines the flotation performance, the addition of hydrogen peroxide into a chamber of a grease trap or dissolved air flotation cell greatly enhances the flotation of suspended solids. When applying hydrogen peroxide to a grease trap without additional polyelectrolyte, the performance can be improved to a level close to that of a chemical free D.A.F. cell. In fact, with the decomposition of hydrogen peroxide forming microbubbles, the grease trap is chemically converted into a D.A.F. cell. The recovered product is very suitable for reuse after rendering.

If hydrogen peroxide is applied together with a polyelectrolyte the performance of the grease trap can be close to that of a D.A.F. cell where chemicals are employed. Hydrogen peroxide has also been tested to improve the performance of a D.A.F. cell. As mentioned above, the formation of very fine oxygen bubbles results in an increased recovery of suspended solids. This effect is obtained in D.A.F. cells with or without polyelectrolyte addition.

CASE STUDIES

In order to illustrate the effects of H_2O_2 in wastewater treatment, examples will be given for each of the aforementioned applications.
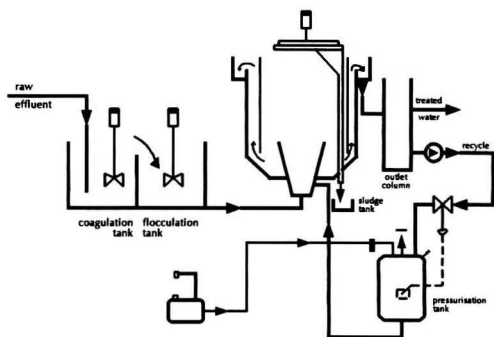
FIGURE 1. D.A.F. cell.
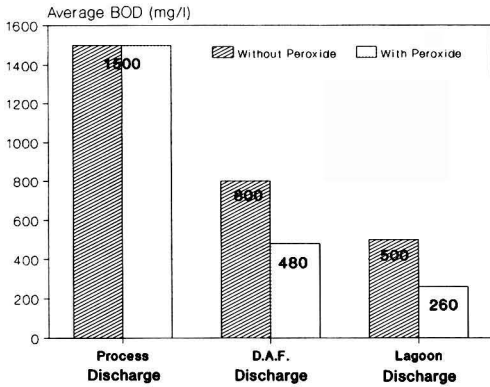
FIGURE 2. Case one—BOD removal.

Case One: H_2O_2 Addition to D.A.F. Cell to Meet Discharge Limits

This poultry/processing plant (180,000 birds processed per day; 2,270 m3 effluent generated per day) chose to use H_2O_2 in their D.A.F. cell in order to meet discharge limits. The treatment system consisted of screens, a D.A.F. cell, an anaerobic lagoon, and ultimate discharge to a POTW (Public Owned Treatment Works). Figures 2 and 3 show the dramatic effects of H_2O_2 addition in terms of BOD reduction and sludge removal.

In this application, by removing more BOD from the wastewater, sludge volume was expected to increase. Instead, because the skimmed-off material was easier to dewater, the injection of H_2O_2 resulted in a 15% decrease in sludge volume (Figure 3). The dry content of the sludge increased from 12% to 20%.

In addition to increased BOD removal, the effluent from the anaerobic lagoon improved substantially. The amounts of polymer and flocculant employed in the D.A.F. cell could also be reduced. This is shown in Table 1.

Case Two: H_2O_2 Addition to Grease Trap to Meet Discharge Limits

The objective at this large processing plant (11,350 m3 effluent per day) was also to lower the BOD to meet discharge limits. The treatment system consisted of screens, a grease trap, an anaerobic lagoon, and discharge to POTW. Figure 4 shows the improved BOD removal achieved with a coagulant, polymer and hydrogen peroxide. The BOD of the final effluent was reduced by more than 50% after converting the system.
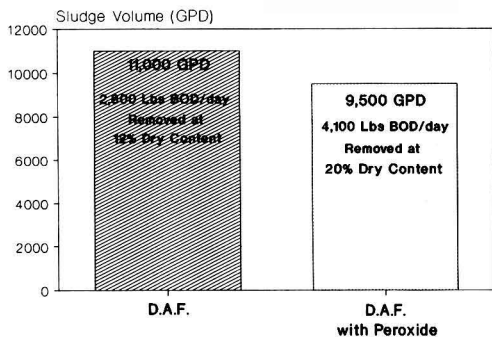
Table 1 Additional Benefits After Three Weeks H_2O_2 in Use

Chemicals Added to D.A.F. Cell	Without H_2O_2	With H_2O_2
Coagulant	240 mg/l	210 mg/l
Polymer	7 mg/l	4 mg/l
Lagoon Discharge		
Ammonia (NH_3)	105 mg/l	65 mg/l
Sulfide (H_2S)	12 mg/l	5 mg/l

Since this grease trap was basically converted into a flotation cell, a dramatic impact on the skimmed material was observed. This is reflected in Figure 5.

Case Three: FOG—Removal

This is a rendering plant with 300 m³/day of wastewater per day. Their treatment system consisted of one grease trap and one D.A.F. cell before using H_2O_2. A polyelectrolyte polymer was employed in the D.A.F. cell resulting in a total FOG recovery of 55% on average. When H_2O_2 was introduced into the raw water of the D.A.F. cell the FOG recovery increased significantly to 90-95%. More importantly the surcharges for excessive FOG discharge were eliminated. The hydrogen peroxide consumption was about 18 kg of 50% H_2O_2 per day. The polymer consumption remained the same as before.

Case Four: FOG—Removal

In a small rendering plant the FOG removal was increased from 20% to over 90% when hydrogen peroxide and a polyelectrolyte polymer were introduced into the grease trap. As illustrated in Table 2 the additional revenue from FOG recovery more than outweighed the chemical.

Case Five: BOD/FOG Removal

This poultry processing plant has a daily effluent flow of 4500 m³/day. Their waste water system consists of one D.A.F. cell. Before they started applying H_2O_2, a very expensive food grade coagulant was used in combination with a polymer for emulsion breakdown and flocculation. At this time the total BOD removal averaged 70-80%. When hydrogen peroxide was added into the D.A.F. cells the BOD recovery yielded 85-90%. Optimization of process parameter and chemicals dosage resulted in total replacement of the coagulant while the polymer consumption remained consistant. As shown in Table 3, the chemical costs were reduced by almost 50% by using H_2O_2.

FIGURE 3. Case one—sludge removal.
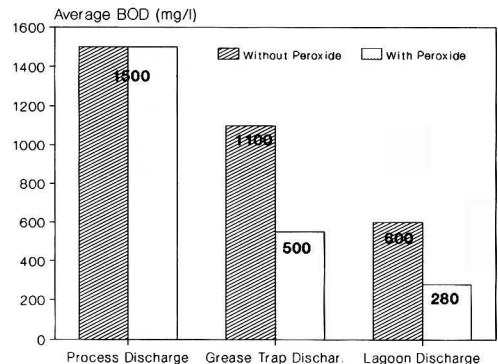
FIGURE 4. Case two—BOD removal.
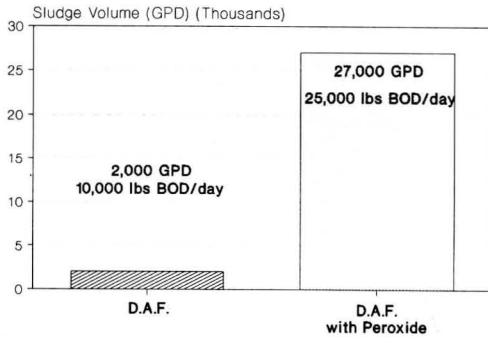
FIGURE 5. Case two—sludge removal.

Table 2 Process Costs

H$_2$O$_2$:	-0.88 US$/m^3
Polymer:	-0.47 US$/m^3
Additional FOG Recovery:	1.40 US$/m^3
Total Benefits:	$+0.05$ US$/m^3

The recovered fat, oil and grease is sold as a food additive in the feed industry. Analysis of the product indicated that no changes in the properties or the composition were caused by the introduction of H$_2$O$_2$ into the process.

Table 3 Chemical Costs (US$/week)

	Before Using H$_2$O$_2$	After Using H$_2$O$_2$
H$_2$O$_2$:	—	1800
Polymer:	4800	4800
Coagulant:	7000	—
Total Costs:	11800	6600

CONCLUSION

Hydrogen peroxide has been shown to be a cost effective reagent for enhanced FOG recovery and BOD removal from wastewater. Many applications in the US and Canada have shown that the process yields a material which is easy to render and suitable for reuse.

Since the process can be easily incorporated into an existing waste water treatment plant design, it is most applicable when improved solids removal is required without major investment costs, such as for emergency situations, during seasonal peaks or periods of increased production.

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Removal of Creosote from Soil by Bioslurry Reactors

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Biological slurry reactors were tested for removal of polynuclear aromatic hydrocarbons (PAHs) from creosote contaminated soil. Five bioslurry reactors, operated in parallel, kept the soil aerated, partially suspended and well mixed. The reactors were inoculated with indigenous microbes of the Genus Pseudomonas. Nutrients were added to maintain the optimum ratio of carbon, nitrogen, and phosphorus. Temperature within the reactors was approximately 25°C. The slurry consisted of approximately 30% contaminated soil. Results of pilot studies showed that approximately 90% of the total PAHs were removed in the first two weeks. Total PAH concentration in the soil was reduced from approximately 10,973 mg/kg to 1,097 mg/kg. Two and three ring PAHs, such as naphthalene, fluorene, and phenanthrene were approximately 96% removed in the first two weeks and higher ring compounds such as chrysene, benzo-a-pyrene, and benzo(b) fluoranthene were approximately 83% removed in the first two weeks.

INTRODUCTION

This study was performed for the U.S. EPA to supply information as part of the database on Best Demonstrated Available Technologies (BDAT) for soil remediation. The database will be used to develop soil standards for Land Disposal Restrictions (LDRs). IT Environmental Programs (ITEP) and ECOVA Corporation, in conjunction with the U.S. EPA's Risk Reduction Engineering Laboratory (RREL), evaluated the performance of pilot-scale bioslurry treatment on creosote contaminated soil. ECOVA performed testing, monitoring, and analysis at the U.S. EPA Test and Evaluation (T&E) facility in Cincinnati, Ohio. IT Analytical Services (ITAS) performed analyses for the critical paramters that will be used in the development of the LDRs.

Biodegradation involves the oxidation of organic compounds by microorganisms. The ultimate goal of biodegradation is to convert organic wastes into biomass and relatively harmless byproducts of microbial metabolism such as carbon dioxide (CO_2), methane (CH_4), water, and inorganic salts. Several biodegradation technologies are available for the remediation of soils and sludges contaminated with organic compounds. These technologies include composting, in situ biodegradation, solid-phase treatment, and slurry-phase treatment. In slurry-phase bioremediation (bioslurry), contaminated soil is excavated and treated in a bioreactor in which the soil is mixed with water to form a slurry. If necessary, nutrients, microorganisms, and surfactants are added to the slurry to enhance the biodegradation process.

For this project the pretreatment soil was analyzed for the Contaminated Soil and Debris (CS&D) List of Contaminants. The organic contaminants that were found were identified as the critical contaminants of interest for this study. These contaminants are listed in Table 1. The contaminants are all aromatic compounds. The volatiles are single ring compounds. The semivolatiles are two to six ring compounds and they are

Table 1 Critical Contaminants of Interest

Semivolatile Organics	Volatile Organics
Naphthalene	2-Butanone
Acenaphthylene	Benzene
Acenaphthene	Toluene
Fluorene	Ethylbenzene
Phenanthrene	Styrene
Anthracene	Total Xylenes
Fluoranthene	
Pyrene	
Benzo(a)anthracene	
Chrysene	
Benzo(b)fluoranthene	
Benzo(k)fluoranthene	
Benzo(a)pyrene	
Dibenzo(a,h)anthracene	
Ideno(1,2,3-cd)pyrene	

listed in order of increasing rings and increasing molecular weight.

This paper is a summary of the full Onsite Engineering Report (OER) [1] that completely describes the operation, sampling, analyses, and results of the pilot-scale study. Results of similar studies on biodegradation of aromatic compounds were published by Versar, Inc., [2] the U.S. EPA [3] and Mueller [4].

PILOT SCALE TREATMENT SYSTEM & PROCEDURES

Reactors

Five EIMCO Biolift™ Reactors each with 64 liters capacity, were used for this study (Figure 1). These reactors are made of stainless steel and equipped with agitation, aeration, and temperature controls. Agitation is provided by three mechanical methods. First, a rake mechanism moves the settled ma-

FIGURE 1. EIMCO Biolift™ reactor.

terial from the bottom of the reactor to the second agitation mechanism, an airlift circulation system that circulates the material to the top of the reactor. The third agitation mechanism is a low-sheer impeller located on the central shaft of the reactor. Aeration is supplied by a set of air diffusers that are attached to the rake arm shaft near the bottom of the reactor. Temperature is controlled by a heat tape system with a digital readout.

The EIMCO Biolift™ Reactor can be sampled in two ways. An opening at the front top of the reactor allows access at the top surface of the liquid. This permits visual inspection of the mechanical actions within the reactor as well as data collection with hand-held instruments that can be inserted into the slurry from the top. Samples are collected from the three sampling ports located along the side of the reactor at three vertical penetrations through the reactor wall. Samples collected from each of the three ports represent three distinct zones of the slurry. The bottom sampling port provides sample material from within the rake mixing zone where the heaviest particles are likely to be present. The middle sampling port provides sample material from within the most well-mixed zone of optimal grain size. Finally, the top sampling port provides sample material from the finest mixing distribution. Samples of the contaminated material, collected by means of these three ports, are crucial in the evaluation of the mechanical efficiency of the reactor.

Sampling

The five bioslurry reactors were operated in parallel and composite samples were collected from each reactor at approximately the same time for pre- and post treatment analysis and throughout the study to monitor system operation. The composited sample from each reactor was made up of portions from each of the three verticle side ports so that the final composited sample contained 30 percent solids. Initially samples were drawn from each of the three ports and the percent dry solids in each port sample was determined. Calculations were performed to determine the volume that was required from each port to provide an overall composite that contained 30 percent solids. Composite sampling ensured that analyses were performed with a representative sample of the entire slurry column. These composite samples were centrifuged to separate the liquid and solid layers and both layers were analyzed for PAHs. Some analyses (e.g., particle size distribution, plate counts) were performed on samples collected from individual ports to determine potential differences among the three slurry zones.

All parameters in this study were monitored in accordance with the sampling schedule presented in Table 2. Week T_0 corresponds to May 8, 1991, and Week T_{12} corresponds to July 31, 1991. The values in Table 2 refer to the volumes of slurry, soil, or water taken for each analysis at each point in time.

Air sampling was also conducted to characterize the off-gases emitted from the bioreactors during the operations and to determine organic constituent loss through volatilization. These samples were collected for information only and were not used to evaluate the technology's performance. All five reactors were vented through stainless steel piping into a manifold system before carbon filtration and eventual exhausting to the outside air. The air monitoring was conducted at a point prior to the collection manifold to obtain emissions from two individual reactors.

Two sampling trains were constructed to collect samples of volatile and semivolatile organics. Volatile organics were collected in a SUMMA passivated canister, and semivolatiles were collected in XAD-2 resin tubes. The XAD-2 resin tubes and canisters were installed in the venting systems for the tested reactors. The XAD-2 resin tubes were analyzed for semivolatile
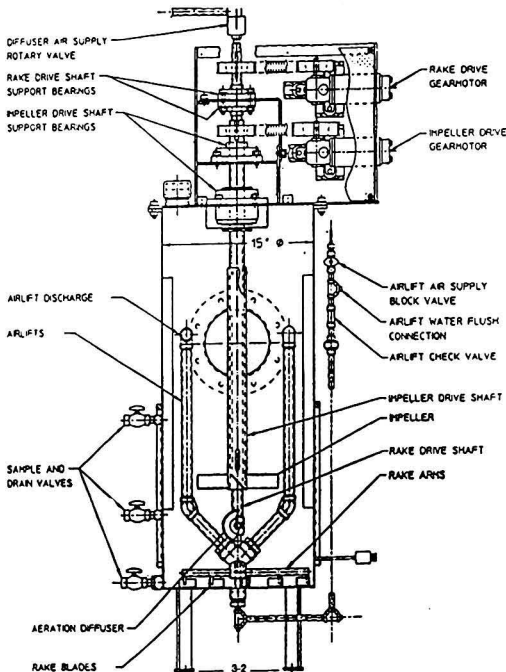
Table 2 Reactor Monitoring Schedule

Sample Volume Per Reactor,
Slurry-Phase Pilot Test

Analysis	0	1	2	3	4	5	6	7	8	9	10	11	12
							Week						
Semivolatile organics (mL)	2000									2000			200
PAH/HPLC-Water/Soil (mL)	60	60	60	60	60		60			60	60	240	60
O&G/TPH (mL)	100		100	100	100		100			100	100	100	100
TOC (mL)	100		100		100		100			100	100		100
Nutrients (mL)	40		40		40		40			40	40		40
Ammonia (mL)	10		10		10		10			10	10		10
Total heterotrophs (mL)	10	10	10	10	10		20			10	10		10
PAH degraders (mL)	10		10		10		20			10	10	10	10
Microtox (mL)	20		20		20					20	20		20
TS (mL)	60	60	60	60	60		60			60	60	60	60
TSS & TVSS (mL)	250		150	70	100		100			100	100	100	100
Dissolved oxygen	DR[a]	DR	DR	DR	DR	DR	DR	DR		DR	DR	DR	DR
Temperature	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR
pH	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR
Total volume (mL)	2660	130	560	300	510	0	510	0	0	2510	510	510	2510
IT vol. per week (mL	2160		100	100	100		100			2100	100	100	2100
Ecova vol. per week (mL)	250	70	250	70	250		250			250	250	250	250
Ecova (T&E facility) (mL)	250	60	210	130	260		160			160	160	160	160
Total volume (L)	64	64	64	64	64	64	64	64	64	64	64	64	64
Sample % solids	30	30	30	30	30	30	30	30	30	30	30	30.0	30.0
Slurry wt. removed (mL)	296	51	218	78	199	0	199	0	0	199	199	199	199
Soil wt. removed (g)	228	39	168	60	153	0	153	0	0	153	153	153	153
Slurry % solids remaining	29.73	29.68	29.48	29.41	29.22	29.22	29.04	29.04	29.04	28.85	28.67	28.49	28.30

[a]DR = Measured using a direct-reading instrument.

organic compounds, and the SUMMA passivated canisters were analyzed for volatile organic compounds.

Soil Particle Size

A major factor of concern from the initiation of the pilot-scale phase was the particle size of the slurried soil. It was important to decrease the settling velocity of the soil by increasing the viscosity so far as to maintain a manageable slurry suspension that could be recirculated within the bioreactors. Also, bioavailability of the soil-bound PAH residues as a function of the path length from the particle surface to the innermost recesses was crucial for maintaining a timely and efficient biodegradation rate. The soil was therefore wet-milled by passing it through a ball mill three times before using it to charge the reactors. Particle-sizing samples were taken before and after milling and at Week T_8. These samples were analyzed in accordance with ASTM D422-62. The resulting comminution of the soil particles is shown in Figure 2. As a percentage of the total solids, soil directly from the site (premilled) had a diameter that was approximately 32% greater than 0.3 mm. After milling (postmilling), the fraction of this soil particle size greater than 0.3 mm was about 8%. Examination of the particle size data (Figure 2) for Week T_8 soil reveals a further phenomenon that must have occurred within the reactors themselves. The percentage of the soil with smaller "particle" size at Week T_8 appears to be greater than that for the pre- or postmilled soil. This indicates a further comminution of the soil particles to a greater fraction of smaller particles within the reactors over time. Comminution increases the viscosity of the slurry and as the number of particles increases, the path length that the PAHs within the soil particles must diffuse to the surface decreases (hence, the mass transfer limitations decrease). This creates greater surface area to which bacteria can attach and adsorb PAHs for metabolism, and probably increases the extraction efficiency of soil-bound PAHs.

RESULTS OF BENCH-SCALE TESTS

Bench-scale tests were performed to determine optimum conditions for the pilot-scale studies. One objective was to determine which combination of nutrients, inoculum, and surfactant would yield the best biodegradation results. These results are shown in Figures 3 and 4. These Figures show that nutrients plus inoculum gave results that were slightly better than nutrients alone and just as good as nutrients, inoculum, and Tween™ (surfactant). Therefore, nutrients plus inoculum were used for the pilot-scale tests. Surfactant was not added because it did not enhance degradation and it would cause additional foaming within the reactors.

A microbial evaluation of the contaminated soil was conducted to determine the size and diversity of bacterial populations and the ability of these organisms to degrade polycyclic

FIGURE 2. Grain diameter (mm).

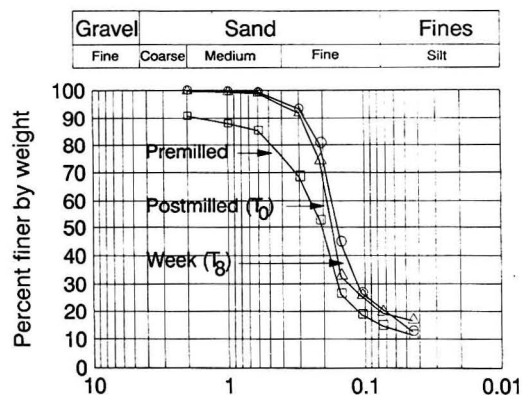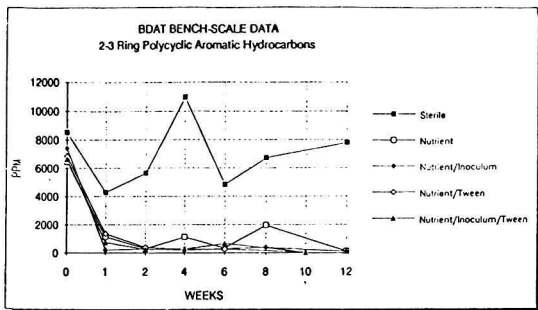**FIGURE 3. BDAT bench-scale data: 2-3 ring polycyclic aromatic hydrocarbons.**

aromatic hydrocarbons. Enrichment culture techniques and selective plating procedures were used to isolate and characterize PAH degrading organisms. Seventeen distinct isolates were identified as having the ability to degrade PAHs. The most prevalent species identified were *Pseudomonas fluorescens* and *Pseudomonas stutzeri*. Three of the isolates were chosen for use in an inoculum on the basis of their broad substrate oxidating range: *Alcaligenes* sp. (CFL-1), *P. stutzeri* (CPH-1), and *P. fluorescens* (CP-3). The pilot scale reactors were inoculated with these PAH degrading organisms at a concentration of 9.3×10^7 per gram of soil. Inorganic nutrient data were collected (table below) to determine whether, based upon TOC, the levels and ratio of N and P were sufficient to support optimal microbial activity.

Baseline Inorganic Chemical Analyses (mg/L)

Analysis	Replicates		Means
Calcium	43.3	44.1	43.7
Magnesium	8.33	8.40	8.37
Potassium	2.72	3.15	2.94
Sodium	5.28	5.12	5.20
Ammonia (NH$_4$-N)	37.5	36.1	36.8
Nitrate (NO$_3$-N)	0.559*	0.565*	n/a
Ortho-Phosphorous (PO$_4$-N)	0.559*	0.565*	n/a
Total Kjeldahl Nitrogen	874.	882.	878.
Total Organic Carbon	34000.	37000.	35000.

*Detectable but below the limit of quantitation

The pilot scale reactors were supplemented initially with ammonia-nitrogen and phosphorus at a TOC:N:P ratio of 100:10:1.
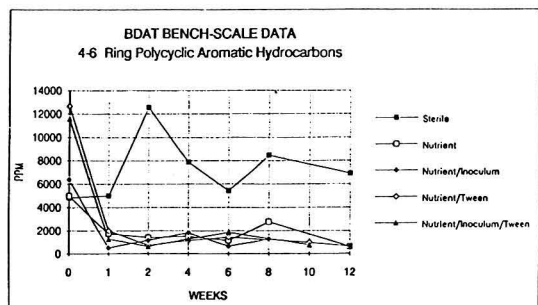
FIGURE 4. BDAT bench-scale data: 4-6 ring polycyclic aromatic hydrocarbons.

Table 3 Baseline Soil PAH Concentrations Average of 5 Reactors (Week T$_0$)

PAH	MEAN (5) mg/kg	Std. Dev. mg/kg
Naphthalene	2143.3	710
Acenaphthylene	17.4	7.6
Acenaphthene	1937.1	1016.8
Fluorene	967.8	288.4
Phenanthrene	518.9	12.1
Anthracene	307.0	34.7
TOTAL 2-& 3-ring PAHs	5891.5	
Fluoranthene	2428.7	732.6
Pyrene	161.1	51.2
Benzo(a)anthracene	957.2	284.8
Chrysene	468.1	129.6
Benzo(b)fluoranthene	389.4	112.7
Benzo(k)fluoranthene	279.6	83.1
Benzo(a,h)anthracene	260.2	75.4
Indeno(1,2,3-cd)pyrene	119.9	94.1
	17.2	4.8
TOTAL 4-6 ring PAHs	5081.4	
TOTAL PAHs	10972.9	

RESULTS OF PILOT SCALE TESTS

Soil Sampling

Table 3 summarizes the results of the baseline (Week T$_0$) characterization of the soil used in the pilot-scale phase of this study. Fluoranthene, naphthalene, and acenaphthene are the constituents present at the highest concentrations followed by fluorene and benzo(a)anthracene. Total PAH concentration in these soils averaged 10973 mg/kg. The 2- and 3-ring PAHs constitute 5892 mg/kg of the total, and the 4-ring and higher PAHs account for 5081 mg/kg.

Total PAH degradation averaged 93.4 ± 3.2 percent over all five operating reactors during the 12-week study (Tables 4 and 5). After only 2 weeks of slurry-phase treatment, total PAH degradation averaged 89.3 ± 3.9 percent for the five reactors. Average degradation rates (mg/kg/wk) for 2- and 3-ring PAHs were appreciably higher at two weeks (95.9 ± 1.8%) than they were for 4 and higher ring PAHs (81.6 ± 3.9%). The more rapid degradation of the lower molecular-weight PAHs reflects the preference of the bacterial populations for these PAHs over the higher molecular-weight PAHs. The final concentrations at week T$_{12}$ averaged 653.5 ± 178.9 mg/kg for total PAHs, 152.1 ± 81.9 m/l for 2- and 3-ring PAHs, and 501.4 ± 103.5 mg/kg for 4- and higher ring PAHs.

Table 4 shows considerable variation in PAH concentration between the 5 reactors. It is important to note that these data reflect not only the nominal concentrations of soil-bound PAHs, but also the extraction efficiency of the analytical method. Apparent increases in the levels of soil-bound PAHs probably reflect an increased PAH extraction efficiency rather than the unlikely production of soil-bound PAHs during the study.

A comparison of 2-3 ring PAHs to 4-6 ring PAHs shows more complete degradation of the 2-3 ring PAHs, whereas, degradation 4- through 6-ring PAHs was less complete. Also, there was less variation between reactors for concentrations of 2- and 3-ring PAHs and more variation between reactors for concentrations of 4- and 6-ring PAHs.

Immediately after sampling at Week T$_9$, Reactors 2 and 4 were reinoculated with fresh bacterial populations, and Reactors 5 and 6 were both reinoculated and amended with the surfactant Tween 80™. Reactor 1 was not amended in any way. Table 4 shows that at Week T$_{11}$, levels of total PAHs in unamended Reactor 1 and Reactors 2 and 4 increased dra-

Table 4 Total, 2-3 Ring and 4-6 Ring PAH Levels (Solid Phases)

BDAT Pilot-Scale Polyaromatic Hydrocarbon Levels

	Week 0	1	2	3	4	6	9	10	11	12
					2-3 Ring PAHs					
Reactor 1	4380.59	64.26	312.25	37.55	682.82	31.66	63.09	56.66	600.95	78.42
Reactor 2	6158.29	970.17	160.72	55.66	247.76	212.93	116.37	72.96	492.38	95.29
Reactor 4	6699.04	2904.45	189.59	41.48	150.26	333.88	124.09	307.52	551.41	104.97
Reactor 5	3758.81	683.53	168.53	85.05	359.75	69.2	85.04	317.95	80.12	249.72
Reactor 6	8460.94	948.59	304.9	144.92	241.23	51.62	183.71	66.04	42.44	232.32
					4-6 Ring PAHs					
Reactor 1	3526.33	2273.11	1043.28	445.29	1734.92	417.93	238.82	470.94	524.9	488.13
Reactor 2	5696.53	3754.18	942.26	480.62	1278.03	1132.16	463.94	552.36	503.44	432.39
Reactor 4	6603.17	11827.2	840.23	409.88	645.52	1830.56	449.57	503.68	481	375.2
Reactor 5	3360.94	2397.9	644.33	559.17	1318.67	1178.01	549.64	449.14	654.13	593.56
Reactor 6	6220.41	3259.33	877.3	1035.39	1035.92	402.25	274.42	498.19	715.29	617.6
					Total PAHs					
Reactor 1	7906.92	3015.94	1355.53	482.84	2417.74	449.59	301.91	527.6	1125.85	566.55
Reactor 2	11854.8	4724.35	1102.98	536.28	1525.79	1345.09	580.31	625.32	995.82	527.68
Reactor 4	13302.21	14731.62	1029.82	451.36	795.78	2164.44	573.66	811.2	1032.41	480.17
Reactor 5	7119.75	3081.43	812.86	644.22	1678.42	1247.21	634.68	767.09	734.25	843.28
Reactor 6	14681.4	4207.92	1182.2	1180.31	1277.15	453.87	458.13	564.23	757.73	849.92

matically; whereas total levels in reinoculated and surfactant-amended Reactors 5 and 6 essentially did not change. By Week T_{12} the total levels in Reactors 1, 2, and 4 had again declined, but total levels in Reactors 5 and 6 increased.

Anomalies in the PAH degradation rates occurred in reactor 4 for 4 and higher ring PAHs at Weeks T_1 and T_6 (Table 4). For these times, the total PAH level was appreciably higher than for the other reactors. Among the individual PAHs, levels of acenaphthene were clearly higher than those of other 2- and 3-ring PAHs at Weeks T_4 and T_{11} (Figure 5). The anomaly may be related to widely varying levels of acenaphthene among the five reactors which was observed from the standard deviation data for acenaphthene. A final anomaly was the surge in both the mean levels and standard deviations for the 4 and higher ring PAHs at Week T_1 (Figure 6). This was not exhibited by the 2- and 3-ring PAHs for that time point.

These anomalies are indicative of several problems and events. Clearly, further comminution of the soil particles accounted for a portion of the rise in soil-bound PAH residues by reducing the resistance to mass transfer. This, in turn, allowed a higher extraction efficiency in the analytical method and, therefore, higher apparent concentrations. Although acenaphthene is an identifiable compound in an analytical method, it is difficult to quantitate accurately. It has the lowest molar extinction coefficient of all the PAHs in ECOVA's analytical method and is therefore the PAH most subject to errors in quantitation. After Week T_2, PAH residue levels were low enough that a small error in the area assessed for acenaphthene could have an enormous effect on the total levels of PAH residues.

Table 5 Total, 2-3 Ring and 4-6 Ring PAH Degradation Rates (Solid Phases)

BDAT Pilot-Scale Polyaromatic Hydrocarbon Levels

	Week 1	2	3	4	6	9	10	11	12
				2-3 Ring PAH Degradation Rate, % Degradation					
Reactor 1	98.53	92.87	99.14	84.41	99.28	98.56	98.71	86.28	98.21
Reactor 2	84.25	97.39	99.10	95.98	96.54	98.11	98.82	92.00	98.45
Reactor 4	56.64	97.17	99.38	97.76	95.02	98.15	95.41	91.77	98.43
Reactor 5	81.82	95.52	97.74	90.43	98.16	97.74	91.54	97.87	93.36
Reactor 6	88.79	96.40	98.29	97.15	99.39	97.83	99.22	99.50	97.25
				4-6 Ring PAH Degradation Rate, % Degradation					
Reactor 1	35.54	70.41	87.37	50.80	88.15	93.23	86.65	85.11	86.16
Reactor 2	34.10	83.46	91.56	77.56	80.13	91.86	90.30	91.16	92.41
Reactor 4	−79.11	87.28	93.79	90.22	72.28	93.19	92.37	92.72	94.32
Reactor 5	28.65	80.83	83.36	60.76	64.95	83.65	86.64	80.54	82.34
Reactor 6	47.60	85.90	83.35	83.35	93.53	95.59	91.99	88.50	90.07
				Total PAH Degradation Rate, % Degradation					
Reactor 1	61.86	82.86	93.89	69.42	94.31	96.18	93.33	85.76	92.83
Reactor 2	60.15	90.70	95.48	87.13	88.65	95.10	94.73	91.60	95.55
Reactor 4	−10.75	92.26	96.61	94.02	83.73	95.69	93.90	92.24	96.39
Reactor 5	56.72	88.58	90.95	76.43	82.48	91.09	89.23	89.69	88.16
Reactor 6	71.34	91.95	91.96	91.30	96.91	96.88	96.16	94.84	94.21
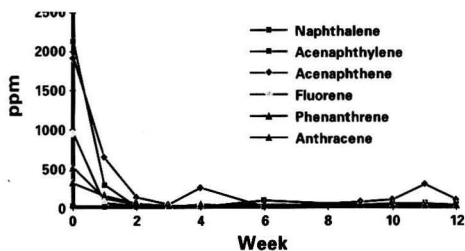
FIGURE 5. 2- and 3-ring PAHs (solids, average of 5 reactors).

FIGURE 7. Total hydrocarbon emission data.

Air Sampling

Air sampling for semivolatile, volatile, and total organics was conducted during the first 9 weeks of treatment. Total hydrocarbon (THC) was determined as methane. This sampling was conducted continuously at the main exhaust line for the first 5 days of operation. Figure 7 is a graph of the THC data during the 5 days of continuous monitor operation. The THC data compare well with the other organic data, showing high emissions the first 2 days of process operation, followed by a steady decline and close to baseline recordings by the fifth day of operation.

Semivolatile organic emissions were sampled on Reactors 1 and 2 for the first 4 days of operation. The main exhaust line was sampled for the remainder of the operation. Table 6 lists the results of semivolatile organic emissions that were detected during the study. Semivolatile organic emissions (naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, dibenzofuran, fluorene, phenanthrene, and anthracene) were detectable during the first 4 days of sampling. Beginning the fifth day of operation, very small quantities (at or below detection)
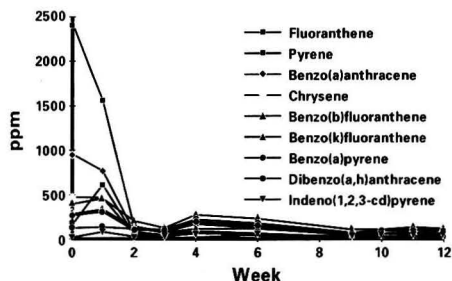

FIGURE 6. 4- to 6-ring PAHs (solids, average of 5 reactors).

of semivolatiles were found. Note that the semi-volatiles were all lower molecular weight 2-and-3 ring compounds. These lower ring compounds were more readily diffused into solution and volatilized. The highest concentration was for naphthalene. These lower ring compounds are easily degraded and Table 6 shows that insignificant concentrations of naphthalene remained after the second day. All of the semivolatiles were below the detection limit after 6 days of operation.

Volatile organic sampling was conducted simultaneously with semi-volatile organic sampling on Reactors 1 and 2 for the first 4 days of operation. The main exhaust line was sampled for the remainder of the program. Table 7 lists the volatile organic concentrations. The table shows that relatively low concentrations of volatiles (mostly benzene, toluene, ethylbenzene, zylenes, and styrene) were detected during the first few days of operation and then dropped off to concentrations that were near the detection limits. This is expected because the volatiles are all lower molecular weight single ring compounds that are very easy to degrade.

Very low to zero concentrations of volatiles were detected in the pretreatment soil and the reason they were detected in the off-gas is probably because they were products of degradation of the higher ring compounds. During the first few days of operation the single ring compounds were being formed more rapidly than they could be assimilated. Table 7 shows that the concentration of volatiles in the off-gas was very low after the fifth day of operation. At this time volatiles were probably being degraded as soon as they were being formed.

CONCLUSIONS

Bench tests were performed first to determine the optimum conditions for the pilot scale tests. Results of the bench tests showed that inoculum plus nutrients should be added for the

Table 6 Semivolatile Organic Emissions Data
(µg/sample)

Compound	SAMPLE NO. - DAY
	XAD1-1	XAD2-1	XAD1-2	XAD2-2	XAD1-3	XAD2-3	XAD2-4	XAD1-5	XAD2-5	XAD1-6	XAD2-6
Naphthalene	8650	8600	98	247	10	20	9	10	10	10	10
2-methylnaphthalene	1500	1559	200	376	10	10	10	10	10	10	10
Acenaphthylene	78	70	55	69	35	64	62	10	10	10	10
Acenaphthene	330	390	360	420	390	500	703	15	15	10	13
Dibenzofuran	170	180	160	160	140	200	230	10	10	10	10
Fluorene	120	110	110	120	140	170	220	10	2	10	10
Phenanthrene	31	33	41	54	41	69	69	10	10	10	10
Anthracene	6	7	8	10	8	13	23	10	10	10	10

Table 7 Volatile Organic Emissions Data (ppb)

	SAMPLE NO. - DAY									
Compound	1-1	2-1	1-2	2-2	1-3	2-3	1-4	1-5	2-5	DL
Benzene	55	45	1.5	2.3	1.8	2.4	1.2	0.79	0.82	0.4
Toluene	240	230	3.2	4.6	5.6	8.0	3.2	2.6	2.2	0.4
Ethylbenzene	150	160	2.2	3.4	0.86	1.5	0.91	0.63	0.5	0.4
m- and/or p-Xylene	720	800	12.0	17.0	0.32	7.3	3.0	1.9	1.4	0.4
o-Xylene	300	320	7.7	14.0	1.4	3.5	1.4	0.7	0.53	0.4
Styrene	44	81	1.8	3.6		0.85	0.45	0.42		0.4

DL = Detection Limit

pilot tests. Surfactant addition did not enhance degradation and it would cause additional foaming. During the bench tests isolates of *Pseudomonas* (*P. fluorescens, P. stutzeri* and *Alcaligenes* sp.) were distinguished as having the best ability to degrade creosote and high concentrations of these indigenous organisms were inoculated into the pilot reactors. During the bench test a TOC:N:P ratio of 100:10:1 was determined. Other minerals, including potassium, magnesium, calcium and iron were added to the pilot reactors.

After two weeks of pilot test treatment, total PAH degradation averaged 89.3%. Degradation of 2- and 3-ring PAHs averaged 95.9% and degradation of 4- and higher-ring PAHs averaged 81.6%. After two weeks of pilot operation, total 2- and 3-ring PAHs were reduced from an average concentration of 5892 mg/kg to 227 mg/kg and total 4- and higher-ring PAHs were reduced from an average concentration 5081 mg/kg to 870 mg/kg.

There was considerable variation between reactors for individual and total PAH concentrations. This variation was higher for higher ring compounds.

Some PAH concentrations (especially for higher ring compounds) appeared to increase from one week to the following week. This is probably due to increased extraction efficiency with time because of additional soil comminution and the longer time required for the heavier higher ring compounds to be worked out of the soil. Very low concentrations of PAHs were detected in the water phase because the organisms are able to degrade PAHs very quickly in this phase.

During the air sampling, low concentrations of volatiles (toluene, benzene, xylene) and low concentrations of lower 2- and 3-ring semivolatiles (naphthalene, fluorene, phenanthrene) were detected for the first few days of operation. All of these contaminants diminished to concentrations that were below the detection limit after 5 days of operation. The lower molecular weight volatile compounds were probably products of degradation of the higher molecular weight compounds because the pretreatment data showed that most of the volatiles were below the detection limit.

ACKNOWLEDGMENT

DISCLAIMER

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Results of Field Demonstrations of a Newly Developed Pilot-Scale Debris Washing System

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Numerous hazardous waste sites in the United States are littered with metallic, masonry, and other solid debris that may be contaminated with hazardous chemicals [for example, polychlorinated biphenyls (PCBs), pesticides, lead, or other metals]. Although the majority of the debris at Superfund Sites has no potential for reuse, decontaminated debris could either be returned to the site as "clean fill" (rather than being transported offsite to a hazardous waste landfill) or, in the case of metallic debris, it could be sold to a metal smelter.

Previous phases of this project have involved the development of a technology specifically for performing on-site decontamination of debris. Both bench-scale and pilot-scale versions of a debris washing system (DWS) have been designed and constructed. The DWS entails the application of an aqueous solution during a high-pressure spray cycle, followed by a turbulent wash cycle. The aqueous cleaning solution is recovered and reconditioned for reuse concurrently with the actual debris-cleaning process, which minimizes the quality of process water required to clean the debris.

This paper presents the results of bench-scale studies and the results obtained during two field demonstrations of the DWS.

INTRODUCTION

Hundreds of hazardous waste sites scattered throughout the United States are littered with miscellaneous man-made objects and remnants thereof as well as residues from naturally occuring items which may be contaminated with hazardous chemicals. These miscellaneous objects and abandoned devices are generally termed "Debris."

Recently EPA published [1] definitions for debris and contaminated debris which are quoted below:

Debris means solid material that:
1) has been originally manufactured or processed, except for solids that are listed wastes or can be identified as being residues from treatment of wastes and/or wastewaters, or air pollution control devices; or
2) is plant and animal matter; or
3) is natural geologic material exceeding a 9.5 mm sieve size including gravel, cobbles, and boulders, or is a mixture of such materials with soil or solid waste materials, such as liquids or sludges, and is inseparable by simple mechanical removal processes.

Contaminated Debris means debris which contains RCRA hazardous waste(s) listed in 40 CFR Part 261, Subpart D, or debris which otherwise exhibits one or more characteristics of a hazardous waste (as a result of contamination) as defined in 40 CFR Part 261, Subpart C.

The land disposal restrictions (LDR) in 40 CFR 268 generally apply to contaminated debris, including such debris generated from corrective actions and closures at RCRA-regulated land disposal sites, remedial and removal actions at Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA or Superfund) sites; and private party clean-ups.

In conjunction with the promulgation of LDRs, the EPA Risk Reduction Engineering Laboratory (RREL) funded a project to develop technology which could be applied on-site for the decontamination of debris. Since the majority of contaminated debris at Superfund and other hazardous waste sites has no potential for reuse, the purpose of a debris decontamination system is to decontaminate the material sufficiently to permit its return to the site as clean fill or, in the case of metallic debris, sold to a metal smelter for reuse.

Since 1987, IT Corporation in conjunction with EPA RREL in Cincinnati, Ohio, have been developing and conducting bench scale and pilot scale testing of a transportable debris washing system which can be used on-site for the decontamination of debris.

During the initial phase of the debris decontamination project, a series of bench-scale tests have been performed in the laboratory for optimization of the process. After the bench-scale evaluation, a transportable pilot-scale version of the Debris Washing System (DWS) was designed, constructed, and demonstrated at a PCB-contaminated site in Hopkinsville, Kentucky, and at a pesticide-contaminated site in Chickamauga, Georgia. This paper discusses the results of bench-scale studies and the results obtained during two field demonstrations of the pilot-scale DWS.

BENCH-SCALE DEBRIS WASHING SYSTEM

Based on the experience gained during the earlier work [2], a bench-scale system (75-liter size) was designed, constructed, and assembled. The bench-scale system consisted of a spray tank, a wash tank, an oil-water separator, and ancillary equipment (that is, heater, pumps, metal tray, etc). The objectives of bench-scale DWS were to assess the ability of the system to remove contaminants from debris and to facilitate selection of the most efficient surfactant solution.

An extensive survey was made of several different types of commercially available cleaning solutions. Five nonionic, nontoxic, low foaming, metal cleaning surfactant solutions (BG-5, MC-2000, LF-330, BB-100, and L-422) were selected for an experimental evaluation to determine their capacity to solubilize and remove contaminants from the debris surface.

Prior to each bench-scale experiment, six pieces of control debris, including three rusted metal plates, a brick, a concrete block, and a piece of plastic, were "contaminated" by dipping each piece into a spiking material consisting of a known amount of used motor oil, grease, topsoil, and sand. The experimental debris were placed in the spray tank on a metal tray and subjected to a high-pressure spray of surfactant solution for 15 minutes. At the end of the spray cycle, the tray was transferred to a high-turbulence wash tank, where the debris was washed for 30 minutes with the same surfactant solution as that in the spray tank. After the wash cycle was completed, the tray was removed from the wash tank and the debris was allowed to air-dry.

Before and after treatment, surface-wipe samples were obtained from each of the six pieces of control debris and were analyzed for oil and grease. Based on the results, BG-5 was selected as the solution best suited for cleaning oily metallic debris.

As part of the continuing investigation into the performance of the DWS, the representative pieces of debris were spiked with a mixture of spiking material (used motor oil, grease, topsoil, and sand) containing representative contaminants (DDT, lindane, PCB, and lead sulfate) and washed in the DWS with the selected surfactant solution. Three trials were performed. Surface-wipe samples of debris from the first two trials were analyzed for PCB, lindane, and DDT. The surface-wipe samples from the third trial were analyzed for total lead content. The results are summarized in Tables 1 through 3. The average overall reductions of PCBs and pesticides achieved during Trials 1 and 2 were greater than 99 and 98 percent, respectively. The overall reduction of lead was greater than 98 percent.

After the completion of the bench-scale debris washing experiments, the cleaning solution was neutralized to a pH of 8 and then pumped through a series of particulate filters and finally through activated carbon. During this treatment, the PCB, lindane, and DDT concentrations in the solution were reduced to <2.0, 0.03, and 0.33 $\mu g/L$, respectively. The concentration of lead was reduced to 0.2 mg/L after treatment.

Table 1 Summary of Bench-Scale Results of Controlled Debris Analyzed for PCBs and Pesticides (Trial 1)

Controlled Debris	Contaminant	Pretreatment ($\mu g/100$ cm^2)	Posttreatment[a] ($\mu g/100$ cm^2)	Percent Reduction
	Lindane	13,800	0.75	99.99
	4, 4′ DDD	1010	3.8 U	≥99.62
	4, 4′ DDT	6710	5.0 U	≥99.93
	PCB-1260	3550	2.0 U	≥99.94
	Lindane	12,500	0.7	99.99
Metal	4, 4′ DDD	1020	3.8 U	≥99.63
	4, 4′ DDT	7610	5.67	99.93
	PCB-1260	3230	2.0 U	≥99.94
	Lindane	12,300	0.7	99.99
	4, 4′ DDD	1020	3.8 U	≥99.63
	4, 4′ DDT	7800	5.0 U	≥99.93
	PCB-1260	2990	2.0 U	≥99.93
	Lindane	12,900	130	98.99
Brick	4, 4′ DDD	1170	4.9	99.58
	4, 4′ DDT	10,100	360	96.43
	PCB-1260	3360	90.4	97.31
	Lindane	14,000	11.1	99.92
Concrete Block	4, 4′ DDD	1240	3.8 U	≥99.69
	4, 4′ DDT	10,200	28.3	99.72
	PCB-1260	3410	15.3	99.55
	Lindane	9370	1.1	99.99
Plastic	4, 4′ DDD	952	3.8 U	≥99.60
	4, 4′ DDT	7120	12.6	99.82
	PCB-1260	2500	23.4	99.06

[a]U indicates that the target compound was not detected at this level.

Table 2 Summary of Bench-Scale Results of Controlled Debris Analyzed for PCBs and Pesticides (Trial 2)

Controlled Debris	Contaminant	Pretreatment ($\mu g/100$ cm^2)	Posttreatment[a] ($\mu g/100$ cm^2)	Percent Reduction
	Lindane	11,800	0.13 U	100
	4, 4′ DDT	9320	2.32	99.97
	PCB-1260	1770	2.0 U	≥99.89
Metal	Lindane	8180	0.31 U	100
	4, 4′ DDT	7540	4.8	99.94
	PCB-1260	1780	2.79	99.84
	Lindane	6150	0.41	99.99
	4, 4′ DDT	5840	2.61	99.95
	PCB-1260	1450	2.0 U	≥99.86
Brick	Lindane	5810	3.49	99.94
	4, 4′ DDT	5660	10.5	99.81
	PCB-1260	1220	4.1	99.66
Concrete Block	Lindane	6440	397	93.83
	4, 4′ DDT	6610	389	94.11
	PCB-1260	1390	66.1	95.24
Plastic	Lindane	10,300	52	99.49
	4, 4′ DDT	8400	223	97.34
	PCB-1260	1620	35	97.84

[a]U indicates that the target compound was not detected at this level.

Table 3 Summary of Bench-Scale Results of Controlled Debris Analyzed for Lead (Trial 3)

Controlled Debris	Contaminant	Pretreatment ($\mu g/100$ cm^2)	Posttreatment ($\mu g/100$ m^2)	Percent Reduction
	Lead	876	6.0	99.31
Metal	Lead	414	6.0	98.55
	Lead	450	<3.0	>99.33
Brick	Lead	508	<3.0	>99.41
Concrete Block	Lead	414	<3.0	>99.27
Plastic	Lead	446	<3.0	>99.33

PILOT-SCALE DEBRIS WASHING SYSTEM

Based on the results obtained from bench-scale studies, a pilot-scale DWS was designed and constructed. The pilot-scale DWS consists of a 1135-liter spray tank; a 1135-liter wash tank; a surfactant holding tank; a rinse water holding tank; an oil/water separator; and a solution-treatment system consisting of a diatomaceous earth filter, an activated carbon column, and an ion-exchange column. The system also includes other ancillary equipment, such as a heater for the 1135-liter spray tank, pumps, particulate filters, a metal basket, and stirrer motor. The process flow diagram for the DWS is presented in Figure 1. The pilot-scale DWS was assembled in a local warehouse and several tests were conducted. After the warehouse testing, the DWS was disassembled, loaded onto a 14.6-meter semitrailer, and transported to the Gray PCB site in Hopkinsville, KY, which was selected for the field demonstration.

DEMONSTRATION OF DWS AT GRAY PCB SITE

The Gray PCB, located in Hopkinsville, KY, covers approximately 10 hectares. From 1968 to 1987 a metal reclaiming facility was operated at the site, which involved open burning of electrical transformers to recover copper for resale. Soil was found to be contaminated with lead and PCBs. On March 19, 1987, representatives from the Kentucky Department of Environmental Protection conducted an inspection at the site and observed the following conditions: 1) the facility was no longer in operation, 2) approximately 70 to 80 burned-out transformers were on site, along with large amounts of other materials, including asbestos-covered pipes, automobiles, and miscellaneous scrap metal, and 3) multiple burn areas and two sink holes were noted.

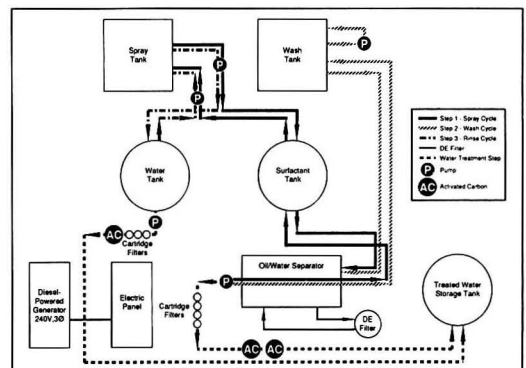The entire DWS was reassembled on a 7.5 m × 7.5 m concrete pad at the Gray PCB site. A temporary enclosure

FIGURE 1. Schematic of pilot-scale Debris Washing System.

Batch Number	Average PCB Concentration on Surfaces ($\mu g/100$ cm^2)			
	Before Cleaning		After Cleaning	
	Average	Range	Average	Range
1	19.7 (N^a = 10)	<0.1–94.0	1.5 (N = 10)	<0.1–9.7
2	9.9 (N = 6)	4.8–17.0	1.5 (N = 6)	<0.1–4.7
3	6.6 (N = 4)	5.0–9.9	1.4 (N = 4)	<0.1–3.3
4	4.1 (N = 6)	<0.1–12.0	0.8 (N = 6)	<0.1–4.1
5	4.0 (N = 8)	<0.1–28.0	<0.1 (N = 8)	<0.1–<0.1
6	2.0 (N = 4)	<0.1–7.8	2.9 (N = 4)	<0.1–10.0
7	2.8 (N = 2)	1.4–4.3	3.9 (N = 2)	<0.1–7.7
8	23.5 (N = 5)	<0.1–70.0	1.3 (N = 5)	<0.1–3.8
9	8.3 (N = 4)	<2.9–23.0	3.1 (N = 4)	1.5–4.9
10	5.2 (N = 4)	<0.1–9.7	1.9 (N = 4)	<0.1–2.8
11	9.4 (N = 4)	<0.1–17.0	3.0 (N = 4)	<0.1–9.5
12	48.8 (N = 4)	2.3–98.0	1.1 (N = 4)	<0.1–3.2
13	12.3 (N = 2)	9.6–15.0	5.1 (N = 2)	<0.1–10.0
14	16.7 (N = 2)	8.7–25.0	<0.1 (N = 2)	<0.1–<0.1
15	18.5 (N = 4)	8.1–27.0	<0.1 (N = 4)	<0.1–<0.1
16	11.3 (N = 2)	8.6–14.0	2.0 (N = 2)	1.5–2.5
17	24.8 (N = 4)	1.1–80.0	2.2 (N = 4)	<0.1–8.4
18	8.4 (N = 5)	<0.1–19.0	3.4 (N = 5)	<0.1–7.4
19	8.3 (N = 4)	<0.1–18.0	3.2 (N = 4)	<0.1–5.3
20	24.0 (N = 3)	13.0–45.0	3.3 (N = 3)	<0.1–9.8
21	18.6 (N = 8)	<0.1–44.0	0.4 (N = 8)	<0.1–2.1
22	25.0 (N = 4)	12.0–35.0	<0.1 (N = 4)	<0.1–<0.1
23	8.6 (N = 4)	1.5–18.0	<0.1 (N = 4)	<0.1–<0.1
24	6.8 (N = 8)	<0.1–31.0	0.3 (N = 8)	<0.1–1.4

[a]N indicates the number of samples.

approximately 7.5 m high was also built on the concrete pad to enclose the DWS and to protect the equipment and the surfactant solution from rain and cold weather. The demonstration took place during December 1989. Ambient temperature at the site during the demonstration ranged from −34 to 10 degrees Centigrade.

Prior to the initiation of the cleaning process, the transformer casings, ranging from 20 to 380 liters in size, were cut into halves with a metal-cutting partner saw. A pretreatment sample was obtained from one half of each of the transformer casings by using a surface wipe technique [3].

The transformer halves were placed into the basket and lowered into the spray tank of the DWS, which was equipped with multiple water jets that blast loosely adhered contaminants and dirt from the debris. After the spray cycle, the basket was removed and transferred to the wash tank, where the debris was immersed in a high-turbulence washing solution. Each batch of debris was cleaned for a period of 1 hour in the spray tank and 1 hour in the wash tank. During both the spray and wash cycles, a portion of the cleaning solution was cycled through a closed-loop system in which the oil/PCB-contaminated cleaning solution was passed through an oil/water separator, and the clean oil-free solution was then recycled into the DWS. After the wash cycle, the basket containing the debris was returned to the spray tank, where it was rinsed with fresh water.

Upon completion of the cleaning process, posttreatment wipe samples were obtained from each of the transformer pieces to assess the residual levels of PCBs. In the case of the metallic debris sampled in this study, the posttreatment wipe sample was obtained from a location *adjacent* to the location of the pretreatment sample. This was necessary because wiping the surface removes the contamination, and if one were to wipe the same surface after cleaning, the results obtained would be biased low. All field demonstration activities described in this paper were governed by EPA-approved Health and Safety and Quality Assurance Plans [4, 5].

The average concentrations of PCBs on the internal surfaces of the transformer casings before and after cleaning are summarized in Table 4. The before-treatment concentrations ranged from 0.1 to 98 $\mu g/100$ cm^2. The posttreatment analyses showed that all the cleaned transformers had a PCB concentration lower than the acceptable level of 10 $\mu g/100$ cm^2.

After treatment of all transformers at the site, the spent surfactant solution and the rinse water were neutralized to a pH of around 8 by using concentrated sulfuric acid. The neutralized surfactant solution and rinse water were treated in the water treatment system, where they were passed through series of particulate filters, then through an activated-carbon drum, and finally through an ion-exchange column. The treated water was temporarily stored in a 3800-liter polyethylene tank pending analysis. The before- and after-treatment water samples were collected and analyzed for PCBs and selected metals (cadmium, copper, chromium, lead, nickel, and arsenic).

The PCB concentration in the water was reduced by the treatment system to below the detection limit of 0.1 $\mu g/L$. The concentrations of each of the selected metals (except arsenic) were reduced to the allowable discharge levels set by the city of Hopkinsville for discharge into the sanitary sewer. Upon receipt of the analytical results of the water, the treated water, which was stored in the holding tank, was pumped into a plastic-covered, 7700-m^3 pile of contaminated soil at the site.

The test equipment was decontaminated with a high-pressure wash. The wash water generated during decontamination was collected and treated in the water treatment system. The system and the enclosure were disassembled and transported back to Cincinnati in a semitrailer.

During this site cleanup, 75 transformers were cleaned in the DWS. All of these transformers were considered to be clean and sold to scrap metal dealers for reuse.

Table 5 Results Obtained in Analyzing Surface Wipe Samples for Benzonitrile ($\mu g/100\ cm^2$)

Batch Number	Sample Number	Benzonitrile	
		Pretreatment	Posttreatment
1	1	180^a (50)^b	ND^c
	2	130^a (50)	ND
2	1	125	117
	2	90	7.8^a (5)
3	1	43	ND
	2	28	ND
4	1	4400	ND
	2	2700	ND
5	1	47000	10^a (5)
	2	22000	7.9^a (5)
6	1	10^a (5)	ND
	2	8^a (5)	ND
7	1	200	ND
	2	320	10^a (5)
8	1	1400	28
9	1	3000	ND
	2	3500	7^a (5)
10	1	22^a (5)	ND
	2	1400	ND

^{a}Estimated result less than 5 times detection limit.
^{b}Numbers in parentheses indicate the minimum detectable concentration of the analyte.
^{c}None detected in excess of the minimum detectable concentration of 5 $\mu g/100\ cm^2$ unless otherwise specified.

Table 6 Results Obtained in Analyzing Surface Wipe Samples for Dicamba ($\mu g/100\ cm^2$)

Batch Number	Sample Number	Dicamba	
		Pretreatment	Posttreatment
4	1	1.9	0.63^a (0.27)^b
	2	3.4	ND
5	1	ND^c	ND
	2	ND	2.6
6	1	ND (2.7)	ND
	2	ND (2.7)	ND (2.7)
7	1	7.3^a (2.7)	1.8
	2	15	2.3
8	1	55	5.7^a (2.7)
	2	13	0.62^a (0.27)
9	1	1.7	0.63^a (0.27)
	2	ND (2.7)	ND
10	1	41	0.30^a (0.27)
	2	180	0.34^a (0.27)

^{a}Estimated result less than 5 times detection limit.
^{b}Numbers in parentheses indicate the minimum detectable concentration of the analyte.
^{c}None detected in excess of the minimum detectable concentration of Dicamba at 0.27 unless otherwise specified.

DEMONSTRATION OF DWS AT SHAVER'S FARM SITE

A second demonstration of the DWS was conducted at the Shaver's Farm drum-disposal site in Chickamauga, Georgia. Fifty-five gallon drums containing varying amounts of a herbicide, Dicamba (2-methoxy-3,6-dichlorobenzoic acid), and benzonitrile, a precursor in the manufacture of Dicamba, were buried on this 2-hectare site. An estimated 12,000 drums containing solid and liquid residues from the manufacture of Dicamba are estimated to be buried here from August 1973 to January 1974. EPA Region IV had excavated more than 4000 drums from one location on the site when this demonstration occurred in August 1990.

The pilot-scale system was transported to this site on a 14.6-meter semitrailer and assembled on a 7.5 m × 7.5 m concrete pad. The temporary enclosure used previously at the Gray site was reassembled to protect the equipment from rain. Ambient temperature at the site during the demonstration ranged from 24 to 41 degrees Centigrade.

The 55-gallon, pesticide-contaminated, empty drums were cut into four sections. Pretreatment surface-wipe samples were obtained from each section. The drum pieces were placed in the spray tank of the DWS for 1 hour of surfactant spraying, then placed in the wash tank for an additional hour of surfactant washing, followed by 30 minutes of water rinsing in the spray tank. The drum pieces were then allowed to air-dry before posttreatment surface-wipe samples were obtained. Ten batches of one to two drums per batch were treated during this demonstration.

The results obtained during this demonstration are summarized in Tables 5 and 6. The data provide an indication of the effectiveness of the DWS technology for removing pesticides and a related contaminant (benzonitrile) from the internal surfaces of excavated drums. Pretreatment concentrations of benzonitrile in surface-wipe samples ranged from 8 to 47,000 $\mu g/100\ cm^2$ and averaged 4556 $\mu g/100\ cm^2$, whereas posttreatment samples ranged from below detection limit to 117 $\mu g/$ 100 cm^2 and averaged 10 $\mu g/100\ cm^2$. Pretreatment Dicamba value ranged from below detection limit to 180 $\mu g/100\ cm^2$ and averaged 23 $\mu g/100\ cm^2$, whereas posttreatment concentrations ranged from below detection limit to 5.2 $\mu g/100\ cm^2$ and averaged 1 $\mu g/100\ cm^2$.

Upon completion of the treatment, the spent surfactant solution and rinse water were treated in the water treatment system. The treated water was temporarily stored in a 3800-liter polyethylene tank pending analysis. The before- and after-treatment water samples were collected and analyzed for benzonitrile and Dicamba. The concentration of benzonitrile in the pretreatment water samples was 250 and 400 $\mu g/L$ (analyzed in duplicate), and the posttreatment concentration was below the detection limit of 5 $\mu g/L$. The concentration of Dicamba in the pretreatment samples was 6800 and 6500 $\mu g/$ L (analyzed in duplicate), and the posttreatment concentration was estimated to be 630 $\mu g/L$ (value estimated due to matrix interferences).

Because the concentration of Dicamba in the posttreatment water sample was 630 $\mu g/L$, the treated water stored in the polyethylene holding tank was pumped into an onsite water-treatment system for further treatment before its discharge into a nearby creek. Although the concentration of Dicamba in posttreatment water was an estimated value, it was decided to send the water to the onsite water-treatment system prior to discharge as a precautionary measure.

The equipment was decontaminated with a high-pressure wash. The wash water generated during this decontamination was collected and pumped into the onsite water-treatment system. The system and the enclosure were disassembled and transported back to Cincinnati in a semitrailer.

CONCLUSIONS

Field-test results obtained using the pilot-scale DWS showed the unit to be both transportable and rugged. Extreme high and low temperatures had little effect on the operation of the equipment. The system was successfully used to remove PCBs from transformer casing surfaces and certain pesticide and herbicide residues from drum surfaces. Although the system has not been proven effective for removal of all types of organic contaminants from the surfaces of debris, results obtained to date are considered promising.

The cleaning solution was recovered, reconditioned, and reused during the actual debris-cleaning process, which minimized the quantity of process water required for the decontamination procedure. The water treatment system was effective in reducing contaminant concentrations to below the detection limit.

The planned progression of this U.S. EPA-developed technology is continuing with design, development, and demonstration of a full-scale, transportable version of the DWS unit.

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An Overview of the Pooled Emission Estimation Program (PEEP) for POTWs

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California Air Toxics "Hot Spots" Information and Assessment Act of 1987 (AB 2588) establishes a program to develop statewide inventory of site-specific air toxic emissions of over 500 compounds. The goals of AB 2588 are to collect emissions data, to identify facilities having localized impact, to ascertain health risks, and to notify nearby residents. Twenty-four agencies with Publicly Owned Treatment Works (POTWs) initiated a voluntary Pooled Emission Estimation Program (PEEP) at 21 facilities for 18 unit processes. For majority of the unit processes, tests were conducted at three different facilities during each round. The target compounds were selected 21 volatile organic compounds (VOCs), formaldehyde and 2,4,6 trichlorophenol. The program collected and analyzed approximately 2060 air samples and 1220 liquid samples to develop emission factors. A QA/QC project plan which included field and laboratory elements were developed and implemented to ensure high quality data. Discussions on the data evaluation procedures, development of emission factors (the ratio of the compound released to the air per total quantity of the compound entering a unit process), estimating VOC emissions from a weir using DO measurements, and an emission factor model for estimating air emissions using liquid/sludge VOC concentrations for liquid, sludge and digester gas handling treatment facilities as listed above are provided.

INTRODUCTION

The California State Air Toxics "Hot Spots" Information and Assessment Act of 1987 (AB 2588) establishes a program to develop a statewise inventory of site-specific air toxic emissions for a list of more than 400 substances, to assess health risks, and to notify nearby residents of significant risks. AB 2588 and the related Criteria and Guidelines Regulation require facilities to prepare emission inventory plans, emission inventory reports, health risk assessment reports, and biennial updates of emission inventories. It is the first of its kind in the United States to address air emissions by publicly owned treatment works (POTWs).

To answer the AB 2588 challenge and to consolidate resources, a Pooled Emission Estimation Program (PEEP) was developed to provide POTWs with improved procedures for estimating air emissions from selected wastewater treatment processes. A total of 25 public agencies formed a Joint Powers Agreement to finance and direct this program. The project responsibilities include development of the source testing protocols, supervision of air and liquid sampling events, audit of air and water analyses, development of emission factors (*EF*) for tested processes and summation of these findings.

The PEEP emission factor (*EF*) is a median value which is a fraction of a target substance released to the atmosphere per total quantity of the mass loading entering a POTW unit process. The PEEP emission factor approach utilizes the following methodology to calculate the air emissions:

$$\text{Emission Rate} = \text{Mass Loading Rate} \times \text{Emission Factor}. \quad (1)$$

This paper presents descriptions of methodologies for testing/sampling, development of *EF*s, and evaluation of *EF* values. It also summarizes the findings of the correlation between the air emissions and oxygen deficiency ratios across weirs. In addition, an example of the PEEP approach to estimate air emission from a typical POTW is presented.

TESTING/SAMPLING PROGRAM

An intensive sampling program was conducted over five months. A total of 152 source testing events were completed. Approximately 2060 air samples and 1220 liquid samples were collected and analyzed to generate the *EF*s for the selected processes.

Unit Process Selection

Eighteen unit processes, which consist of aerated processes, quiescent basins, gas handling facilities, and sludge handling facilities, were included in the PEEP field testing. The 18 unit processes tested are listed in Table 1.

Field Testing Site Selection

Once the unit processes were selected, from one to seven sites were selected for source testing. A total of 20 field testing agencies (FTAs) were selected or volunteered for participation in the PEEP source testing events. Sites were selected based on their operational configuration, ease of testing, isolation from emissions control devices and their willingness to participate in the program. These facilities are located across the state. Plant sizes range between 3 and 380 million gallons per day (mgd) and represent a total flow of 1.6 billion gallons per day. Individual source testing protocols were developed for each site. Then three rounds of source testing were conducted at the majority of these sites.

Target Substances

After several meetings with the PAs and air management districts, in which substance origin, detection and fate were discussed, the target volatile organic compounds (VOCs) shown in Table 2 were selected for inclusion in PEEP. For combustion processes such as IC engines and boilers, the list of compounds was similar to that for non-combustion processes with noted exceptions. Three additional compounds, 1,3-butadiene, acrolein, acetaldehyde, were included because they were expected to be generated as combustion byproducts. 2,4,6-trichlorophenol was omitted because it was not expected to be found in digester gas or combustion exhaust gas.

Following one complete round of source testing at 50 unit processes, air- and liquid-phase data were evaluated to determine the suitability of the original list of compounds for testing. The glycol ethers and 2,4,6-trichlorophenol were never detected in air or liquid samples. These compounds were dropped from testing for Rounds 2 and 3.

Table 1 Summary of Tested Processes

AERATED PROCESSES	QUIESCENT BASINS
Aerated Grit Chambers	Primary Sedimentation Tanks
Diffused Air Activated Sludge	Secondary Clarifiers
Mechanically Mixed Air Activated Sludge	Tertiary Filters
Pure Oxygen Activated Sludge	Chlorine Contact Tank
	Dechlorination
Trickling Filters	Gravity Thickeners
Dissolved Air Flotation Thickeners	
GAS HANDLING FACILITIES	SLUDGE FACILITIES
	Belt Filter Presses
Anaerobic Digesters	Sludge Centrifuges
IC Engines	Sludge Drying Beds
Boilers	

Table 2 Summary of Target VOCs

Benzene	Perchloroethylene
Carbon Tetrachloride*	Styrene
Chloroform	Trichloroethylene
p-Dichlorobenzene	Trichlorofluoromethane*
1,4-Dioxane	Toluene
Ethylene Dibromide*	1,1,1-Trichloroethane
Ethylene Dichloride	Vinyl Chloride
Glycol Ethers**	Vinylidene Chloride
Methylene Chloride	Xylenes

*Added for Rounds 2 and 3.
**Dropped after Round 1.

Sample Duration

The length of the sampling time was selected for each unit process to allow collection of a representative composite sample. To account for the process fluctuations, air and liquid sampling durations were chosen to span at least three times the normal hydraulic retention time of the process. The sampling durations were as follows: IC engines and boilers, 1 hour; mechanically mixed and diffused air Activated Sludge, 24 hours; all other processes, 8 hours.

Air samples were taken continuously for the entire sampling duration. For liquid samples, grab samples were collected every hour (8 hour duration) or every 2 hours (24 hour duration) and flow composited by the analytical laboratories prior to analysis.

Sampling and Analytical Methods

Air

Three separate air sampling and analytical methods were used for PEEP source testing corresponding to the types of the target compound. Tedlar bags were used for sampling all the volatile organic compounds, dinitrophenylhydrazine (DNPH) coated sepak cartridges for sampling aldehydes and two impinger trains for sampling 2,4,6-trichlorophenol. The sampling and analytical methods are summarized in Table 3. The sampling train for combustion processes is similar to that for non-combustion processes except that the impinger train for 2,4,6-trichlorophenol was deleted.

The induced-air floating flux chamber (or hood) technique was used for sampling the open quiescent basin surfaces of such processes as secondary clarifiers, tertiary filters and chlorine contact tanks. The hood was constructed of 16 gage 316 stainless steel and has overall dimensions of 4 feet (1.25 m) by 5 feet (1.5 m) with a gas sampling area of 8.75 square feet (1.9 square meters). Prior to sampling, but after placing the chamber in the basin, sufficient cylinder air (<0.05 ppm as total hydrocarbon) was introduced to ensure three complete flushes of hood air space. Then the flow rate of supply air was lowered to achieve approximately two hood air space changes per hour. For off-gas sampling from unducted diffused aeration tanks, the cylinder supply air was not required since the plant supply air to the aeration process was sufficient to induce air changes within the sampling hood.

Liquid

Stainless steel beakers were used to collect liquid grab samples. Liquid composites were prepared by the analytical laboratory from each set of grab samples based on process (liquid) flow rates at the time of sample collection.

For all compounds, except 2,4,6-trichlorophenol and glycol ethers in liquid samples, trip blanks for both air and water

Table 3 Summary of Sampling and Analytical Methods

Fraction	Air Sampling	Air Analytical Method	Liquid/ Sludge Sampling	Liquid/ Sludge Analytical Method
VOCs	CARB 422	EPA TO-14	SW 846	EPA 624
Aldehydes	EPA TO-11	EPA TO-11	SW 846	EPA Region 9 HPLC
2,4,6-Trichloro-phenol	EPA TO-8	EPA TO-8	SW 846	EPA 625
Glycol Ethers	CARB 422	EPA TO-14	SW 846	EPA 625

samples were taken on each sampling day and analyzed for any contamination from container preparation, transportation, sample handling or the environment.

Sampling Locations

A site specific testing protocol was developed for each testing site. Figure 1 is a schematic of the typical locations for liquid and air sampling used in this study. The general objective was to develop a sampling protocol which would determine the loading and loss from a particular unit process prior to any air emission control devices. These protocols had to be acceptable by seven California air districts. Generally, for the liquid processes, streams with high suspended solids (greater than 2 percent) were not analyzed because of the resultant high detection limits for these particular samples.

PEEP EMISSION FACTOR DEVELOPMENT

Methods used to derive emission factors for three categories of unit processes are described in this section.

Covered and Ducted Liquid Processes

For covered and ducted processes, both liquid and air samples were collected at the process influent and effluent and were analyzed for the target list of substances. Air emissions were calculated as the difference between the mass of the influent air and the effluent air. The mass carried by each air stream was the product of the concentration, C_{air}, and the corresponding air flow rate, Q_{air}. Therefore, the rate of air emission, E, can be calculated as:

$$E = (Q_{air,out} \times C_{air,out}) - (Q_{air,in} \times C_{air,in}) \quad (2)$$
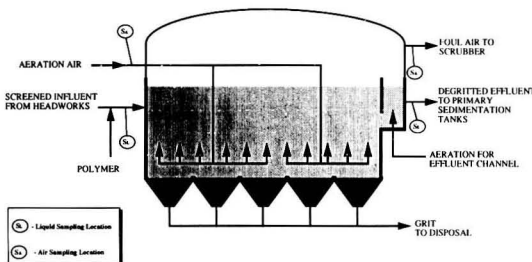

FIGURE 1. Sampling schematic of aerated grit chamber county sanitation districts of Los Angeles County water pollution control plant.

The mass loading, ML, to a process is the product of influent liquid concentration, $C_{liq,in}$, and the process flow rate, $Q_{liq,in}$:

$$ML = (Q_{liq,in} \times C_{liq,in}) \quad (3)$$

The emission factor, EF, is the fraction of the total mass loading of the influent liquid stream which is removed from the process through volatilization. Consequently, the EF can be shown as:

$$EF = \frac{E}{ML} \quad (4)$$

Uncovered Liquid Processes

For the processes which were not covered, floating flux chambers, or hoods, were used to collect emissions from quiescent basins and aeration basins. For flux chamber sampling, supply air of known concentration was fed from a gas cylinder at a flow rate to achieve at least two air space exchanges within the hood per hour. The air emission from the process can then be calculated by:

$$E = \left(\frac{A}{8.75}\right)(Q_{hood})(C_{hood,out} - C_{in}) \quad (5)$$

where A is the total surface area of the tank in sf, 8.75 sf is the surface area measured by the hood and C_{in} is the concentration of the target compound in the cylinder air. The EF from the process was then determined by inserting equation 5 into equation 4.

For the diffused air activated sludge process, the air flow from the process provided sufficient air changes without additional cylinder air. The air emissions from the process can be calculated by:

$$E = \left(\frac{A}{8.75}\right)(Q_{hood})(C_{hood,out} - C_{air,in}) \quad (6)$$

where $C_{air,in}$ is the concentration in the supply air to the aeration tanks. The EF from the process was then determined by inserting equation 6 into equation 4.

Combustion Processes

For combustion processes using digester gas, that is, IC engines and boilers, the mass loading to the equipment is defined as the total amount of the compound present in the influent streams, digester feed-gas and inlet air. Therefore ML can be calculated by:

$$ML = (Q_{digester\ gas,in} \times C_{digester\ gas,in}) + (Q_{air,in} \times C_{air,in}) \quad (7)$$

Air emissions from the combustion processes are the product of the exhaust air flow rate and the corresponding concentration, i.e.:

$$E = (Q_{exhaust\ air} \times C_{exhaust\ air}) \quad (8)$$

The EF can be calculated by dividing equation 8 by equation 7.

In addition to the methodology described above, EF for IC engines can also be expressed in terms of air emission rates per unity of energy output. The EF is calculated by dividing equation 8 by the engine horsepower output. Due to unavailability of the true energy output, design horsepower output was used.

EVALUATION OF EMISSION FACTOR VALUES

A data base was created to facilitate data storage, retrieval and evaluation. Process parameters, such as air and liquid flow rates, analytical results such as air and liquid concentrations and analytical detection limits were included in the database. The data generated during those field tests are summarized in approximately 200 sheets.

Data Averaging Procedures

During source testing, air samples were always collected and analyzed in duplicate; duplicate liquid grab samples were flow composited and the duplicates analyzed at about a 30% frequency. The goal was to compute an arithmetic average for a set of duplicate analyses. Analytical results did not always permit computation of an arithmetic average. This situation arose due to the relatively low concentrations of compounds of concern at POTWs. Treatment of duplicate analytical results can be categorized in three cases.

Case 1: Both Concentrations Above Detection Limit

If the duplicate analyses resulted in two positive values, the concentrations were averaged.

Case 2: One Concentration Above and One Below Detection Limit

If a set of duplicates showed one concentration above and one below the detection limit, the value below the detection limit was set at 1/2 detection limit. An arithmetic average of the positive value and 1/2 the detection limit was used in subsequent evaluations.

Case 3: Both Concentrations Below Detection Limit

If the duplicate analyses resulted in two negative detections, that is, not detected, the concentration was assumed to be zero.

Data Qualification Procedures

Before determining the final EFs, it was necessary to evaluate the data generated during the source testing events. A series of qualifying statements were developed for the raw data. The purpose of these statements or comments, is to provide the

FIGURE 2. Frequency distribution of EFs from aerated grit chamber.

user with an evaluation tool for each calculated emission factor. The individual computed EF values for each source test were disqualified from the final averaging process, if they were associated with one of two data flags.

The first data flag applies if either the effluent air or influent liquid concentration was less than three times the corresponding detection limit. This QA/QC procedure was made based on the fact that the accuracy and precision of the reported value become more questionable as the concentration approaches the limit of detection of the instrument.

The second data flag applies if the effluent air or inlet liquid concentration was less than three times the concentration reported in the corresponding trip blank. Air and liquid trip blanks at each sampling site traveled and were analyzed at the same time as the samples. This QA/QC procedure was intended to detect contamination due to shipping, storage and environmental handling of samples prior to analysis.

Selection of the Median Value

The EF values derived during PEEP were based on air and liquid concentrations measured in the field under normal operating conditions. Investigators in various environmental fields have reported that concentrations of substances measured in the environment often have frequency distributions that are log normal [1]. That is, when the cumulative probability of "measurements" are plotted on log probability paper, the resulting plot is a straight line. It was hypothesized that PEEP EFs should be log normally distributed. To test this hypothesis, the cumulative probability of the log 10 of the EFs for chloroform and perchloroethylene (PCE) in aerated grit chambers was plotted as shown in Figure 2. The data in Figure 2 appear to fall on two straight lines. This confirms that the EFs are log normally distributed.

Close examination of the median and geometric mean indicated that these two values are very similar. The median is a good estimate of the geometric mean, especially when there are zero values and small sets of EFs.

Examples of the EF's

An example of the computed EF for aerated grit are summarized in Table 4. The blank values resulted from data which were flagged or the EF could not be computed due to the cases described above. Negative values were permitted into the database. Under these conditions, the compounds were either formed due to reactions in the treatment process such as chloroform due to chlorination at the headworks to eliminate odors or the return activated sludge line to halt bulking.

Due to the lack of computed EFs for all the target compounds, estimated EF were provided to allow a POTW to estimate emissions for target compounds with no computed EF's. The chlorinated and non-chlorinated compounds were grouped. The median computed EF value was determined. These values were used as estimated EF's for the chlorinated and non-chlorinated compounds, respectively. An example of the estimated EF's for the aerated grit process is presented in Table 5. The non-bolded numbers are computed EF's, and the estimated EF's are bolded.

EF Reasonableness Check

PEEP EFs were compared with the results of the Environment Canada 4 plant study [2, 3, 4] to determine whether the PEEP results were reasonable. Though smaller in scale, the Environment Canada study was the most similar, of all the available studies in literature, to the PEEP methodology. Four plants were tested by a single group using the same protocol at all the sites. Additionally, this report contained a relatively
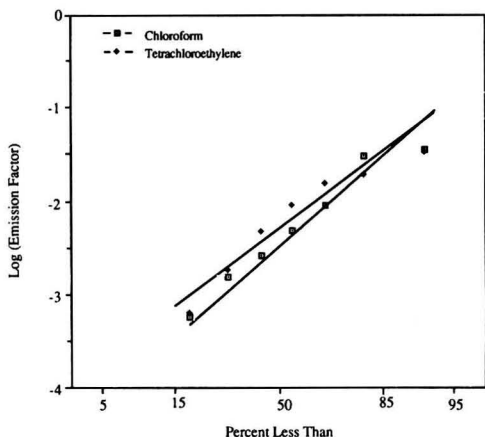
Table 4 Summary of Emission Factors for Aerated Grit Chamber

Compound	Emission Factors									Number of EFs	Median
	Round 1			Round 2			Round 3				
	A	B	C	A	B	C	A	B	C		
Benzene	8.9E−3			3.2E−2			3.6E−2			3	3.2E−2
Carbon Tetrachloride											
Chloroform	4.8E−3	1.5E−3	2.6E−3	3.0E−2	5.6E−4		3.5E−2	0.0E+0	8.9E−3	8	3.7E−3
Dichlorobenzene	0.0E+0	0.0E+0		−7.3E−4				0.0E+0	1.5E−3	5	0.0E+0
1,4-Dioxane											
Ethylene dibromide											
Ethylene dichloride											
Methylene chloride	2.8E−3		1.5E−3	3.3E−2	6.1E−4	9.0E−3	1.9E−2	0.0E+0	1.5E−2	2	2.1E−3
Tetrachloroethylene	1.8E−3		4.7E−3							8	6.8E−3
Styrene											
1,1,1-Trichloroethane	1.1E−2	2.0E−3		7.4E−2	8.4E−4		2.4E−2			5	1.1E−2
Trichloroethylene						7.7E−3			1.3E−2	2	1.0E−2
Trichlorofluoromethane						0.0E+0				1	0.0E+0
Toluene	1.9E−3	7.4E−4		2.4E−2	6.5E−4		1.7E−2	−9.7E−5		6	1.3E−3
Vinyl chloride											
Vinylidene chloride											
Xylenes	3.4E−4			7.5E−3	2.5E−4		−2.8E−3	−7.1E−5		5	2.5E−4
Formaldehyde	−6.1E−6		−6.8E−6							2	−6.4E−6

A: JWPCP
B: CSDOC
C: ENCINA

broad data base and allowed a parallel comparison with the PEEP data base. The Environment Canada study considered only two processes: aerated grit chambers and activated sludge basins.

A two-step reasonableness check was performed. Firstly, each study was compared with an established environmental parameter, fraction of saturation, to determine whether the data were independently reasonable. The fraction of saturation is the ratio of off-gas concentration to the gas concentration in equilibrium with the wastewater in the tank [2]. Secondly, the EFs developed in the two studies were compared.

The data generated from the PEEP and the Environment Canada studies appear to behave similarly and are accepted as reasonable based on the following list of factors [4]:

- Calculated off-gas fraction of saturation values are within the expected range;
- Similar lack of correlation with Henry's constant and air to water ratio are indicated from both studies; and
- EF values obtained in both studies are in the same general range for the aerated grit chamber and the activated sludge process.

Emission Factor Rating

EPA rates the emission factors in its "Compilation of Air Pollutant Emission Factors," [5] using an "A" through "E" grading system, with "A" being the best. In general, factors based on many observations or on widely accepted test procedures are assigned higher rankings. For instance, an emission factor based on ten or more source tests at different plants would likely get an "A" rating. Conversely, a factor based on a single observation of questionable quality, or one extrapolated from another factor or a similar process, would probably be labeled "D" or "E." Each EF developed during PEEP is the median value of three to nine source tests from the same unit process at one to seven different testing sites. Based on the EPA criteria, the emission factors developed by this program approach an "A" rating.

EMISSION FACTOR DETERMINATION FOR WEIRS

A weir is a relatively common component of many unit processes at POTWs. Liquid-phase data were collected for weirs in 19 source tests. Upstream and downstream samples were collected and analyzed for the target list of compounds and dissolved oxygen concentrations. These data were evaluated to determine whether a correlation could be made between organic chemical emissions and DO concentrations.

Several volatilization models developed in the literature are based on the relationship between the oxygen transfer rate and the volatilization rate of organics from weirs [6, 7, 8]. However, these models have not been validated by actual field measurements. In addition, predictions by various models use can differ significantly [9]. Nakasone developed an empirical model to describe weir aeration and he defined the oxygen deficit ratio as [10]:

$$r_o = \frac{C_s - C_u}{C_s - C_d} = \frac{D_u}{D_d} \qquad (9)$$

where: r_o = Oxygen deficit ratio;
C_s = Saturated DO concentration, mg/L;
C_u = Upstream DO concentration, mg/L;
C_d = Downstream DO concentration, mg/L;
D_u = Upstream DO deficit, mg/L; and
D_d = Downstream DO deficit, mg/L.

Similarly, for a given volatile organic compound (VOC), a similar concentration ratio can be defined as:

Table 5 Summary of Estimated and Computed EFs for Aerated Grit Chamber

Target Compound	Aerated Grit Chamber
Benzene	3.2E − 02
Carbon Tetrachloride	**3.7E − 03**
Chloroform	3.7E − 03
Dichlorobenzene	0.0E + 00
1,4-Dioxane	**1.3E − 03**
Ethylene dibromide	**3.7E − 03**
Ethylene dichloride	**3.7E − 03**
Methylene chloride	2.1E − 03
Tetrachloroethylene	6.8E − 03
Styrene	**1.3E − 03**
1,1,1-Trichloroethane	1.1E − 02
Trichloroethylene	1.0E − 02
Trichlorofluoromethane	0.0E + 00
Toluene	**1.3E − 03**
Vinyl chloride	**3.7E − 03**
Vinylidene chloride	**3.7E − 03**
Xylenes	2.5E − 04
Formaldehyde	− 6.4E − 06

Notes: Extrapolated values are in bold-face type.
Negative emission factor implies sorption of compound from air into liquid.
Emission factor is provided in a base 10 format: 1.0E − 2 = 1.0 × 10 − 2 = 0.01.

$$r_v = \frac{\text{Upstream VOC Concentration}}{\text{Downstream VOC Concentration}} = \frac{C_u^{\text{voc}}}{C_d^{\text{voc}}} \qquad (10)$$

The VOC and DO deficit ratios, r_v and r_o, are related by the following equation [6]:

$$\ln(r_v) = (\ln(r_o)) \left(\frac{K_{Lv}}{K_{Lo}} \right) \qquad (11)$$

where: K_{Lv} = VOC mass transfer coefficient, per hour; and
K_{Lo} = Oxygen mass transfer coefficient, per hour.

By converting the equation from the natural log format, and replacing the mass transfer factors indicated above with this relationship:

$$\Psi = \frac{K_{Lv}}{K_{Lo}} \qquad (12)$$

The formula can be simplified as:

$$r_v = r_o \Psi \qquad (13)$$

For surface aeration, Roberts et al. in 1984 concluded that Ψ is equal to 0.60 ± 0.06 for a wide range of organics [11].

To utilize equation 13 in source test data analysis, it is necessary to develop a relationship between equation 13 and the computed EFs. If one assumes a simple mass balance across a weir, where organics are not created or destroyed, and volatilization is the only removal mechanism, the following relationship exists:

$$QC_u^{\text{voc}} - QC_d^{\text{voc}} = \text{Air Emissions} \qquad (14)$$

where: Q = Flow rate, mgd;
C_u^{voc} = Upstream VOC concentration, mg/L; and
C_d^{voc} = Downstream VOC concentration, mg/L.

The total mass loading (ML) is calculated as the product of flow rate (Q) times concentration (C). Referring to equation 10, where the VOC deficit ratio, r_v, is defined, the EF could be related to the change in VOC concentration from the up-

stream sample point to the downstream sample point, and thus, the deficit ratio:

$$EF = \frac{QC_u^{voc} - QC_d^{voc}}{QC_u^{voc}} = 1 - \frac{C_d^{voc}}{C_u^{voc}} = 1 - \frac{1}{r_v} \qquad (15)$$

The emission factor is therefore related to the oxygen deficit ratio by:

$$EF = 1 - \frac{1}{r_o^{\Psi}} \qquad (16)$$

*EF*s were calculated using a liquid-phase mass balance based on measured downstream and upstream VOC concentrations for all of the weirs tested. Figure 3 presents a comparison of the emission factors for all compounds calculated from liquid-phase mass balance with the relationship $(1 - 1/r_o^{0.6})$. According to this equation, the data should lie along a 45° line. Although the general trend is followed, the fit is less than satisfactory.

Figure 4 presents the same comparison for three compounds, chloroform, PCE, and formaldehyde. These compounds were selected based on the relative abundance of the data as compared with other compounds. The compounds are shown separately, for easy comparison. This figure shows that the majority of the data is clustered about the 45° line. There are outliers, as is expected due to the log normal distribution of the data. On inspection, the data fit the equation reasonably well.

In some instances, the weir portion of the process was covered and ducted, for these cases, *EF*s were calculated based on air data. Figure 5 presents a comparison of the *EF*s calculated using a liquid-phase mass balance and those calculated using air data with the relationship $(1 - 1/r_o^{0.6})$. The air-based *EF*s were consistently smaller, by a substantial margin, than those based on liquid-phase mass data. For most compounds, liquid-phase concentrations were near the detection limit, introducing a wide variation in the *EF*s. Based on this figure, the *EF*s calculated from air data appear to present a more realistic trend than those based on liquid-phase mass balance.

In an attempt to better fit the air-based *EF*s to the model, equation 16 was solved for Ψ:

$$\Psi = \frac{\ln(1 - EF)}{\ln\left(\frac{1}{r_o}\right)} \qquad (17)$$

By averaging the resultant values, Ψ was found to be 0.17 for the existing data set. Figure 5 presents a comparison of the air-based *EF*s calculated using this constant, with the relationship $(1 - 1/r_o^{0.17})$. On inspection, the figure shows a good fit of the data to the model.

EXAMPLE AIR EMISSION ESTIMATE FOR A TYPICAL 1.25×10^4 m³/DAY (3.3 MGD) POTW

*EF*s can be used to estimate air emissions from a typical POTW. For example, the following unit processes were selected for liquid handling: aerated grit chamber, primary sedimentation tank, diffused air activated sludge, secondary clarifier, tertiary filter, chlorine contact tank, and dechlorination. The solid and gas treatment trains which were selected are: gravity thickener, anaerobic digesters, belt presses, and an IC engine without NOx controls.

Further, the POTW has the following operation conditions. The inlet liquid flow rate is assumed to be 1.25×10^4 m³/Day (3.3 mgd). The toluene concentration is 100 ppb (μg/L) entering the aerated grit chamber. The sludge flow rate to the
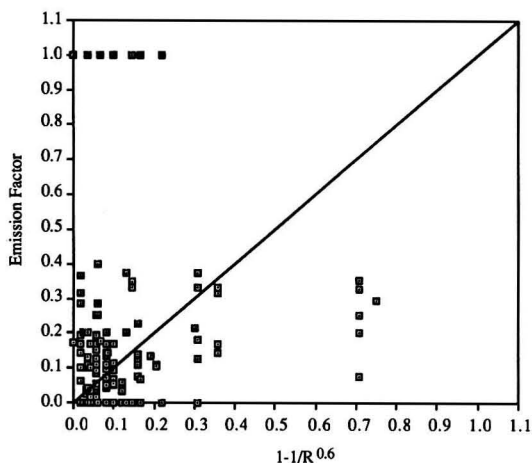
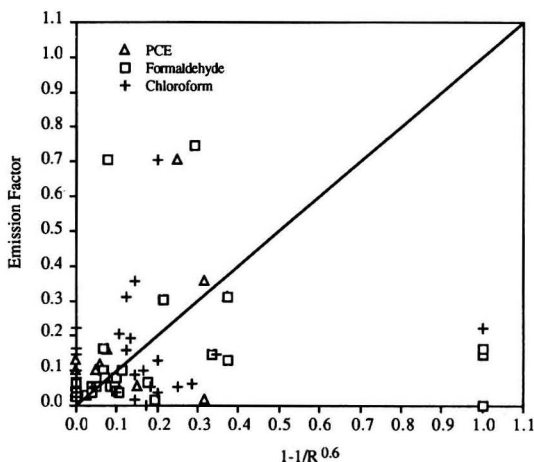FIGURE 3. Correlation between *EF* using liquid data and oxygen deficit ratio (all compounds).

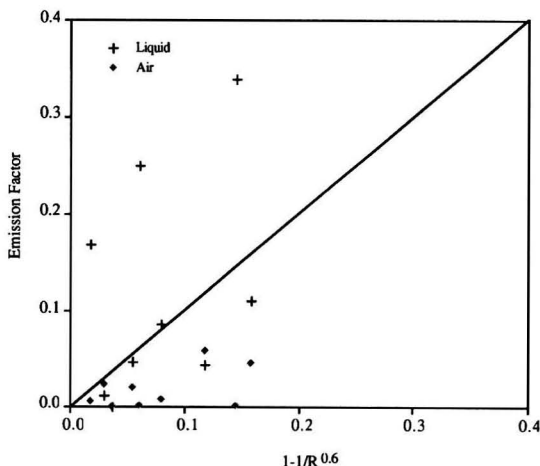FIGURE 4. Correlation between *EF* and oxygen deficit ratio (liquid data).

FIGURE 5. Correlation between *EF* and oxygen deficit ratio (liquid or air data at covered weirs).

gravity thickeners is $2.5 \times 10^3 \, \text{m}^3/\text{day}$ (0.66 mgd) with a toluene concentration of 20 ppb.

Estimating Liquid Concentrations

The liquid flow rate is usually measured continuously, or at least daily, at a POTW. However, the liquid at sludge streams may not be analyzed regularly at all individual processes. It may be costly and sometimes impossible due to inaccessibility of the desirable sampling locations. To alleviate the problem, total mass loss factors (TLFs), derived from PEEP data can provide an estimation method for the concentration of target compounds rather than site specific data from each inlet to a unit process.

The liquid stream data collected for PEEP allows the determination of mass loss of target organics across unit processes. A simple mass balance, using liquid concentrations across a unit process at a wastewater treatment plant, is the total net loss or gain of target organics within a unit process. The loss is the sum of the removal due to sorption, volatilization, biodegradation, and chemical oxidation. The gain is the sum of compounds formed within the liquid- or solid-phase or removal of target compounds from the air stream by sorption into the liquid stream within a unit process. Generally, the influent and effluent liquid flow rates are assumed to be the same, unless a considerable amount of solids are removed as another effluent stream.

The total loss factor (*TLF*) can then be determined using the liquid influent and effluent concentrations. The equation used to calculate the (*TLF*) is as follows:

$$TLF = [(C_{inf} - C_{eff})/C_{inf}] \tag{18}$$

where C_{inf} is the influent concentration, C_{eff} is the effluent concentration and the total loss factor is calculated as a fraction on a weight/weight basis. The calculated *TLF* can then be used to estimate the mass loading to the next liquid process:

$$\text{Mass to Next Process} = (1 - TLF) \times ML \tag{19}$$

Air Emission Estimates for Liquid Handling Systems

*EF*s and *TLF*s for each compound are presented in the PEEP final report. Figure 7 presents a schematic which summarizes the fate of toluene in the process. Moving left to right, the first number is the calculated concentration entering the process. The next section of the diagram describes the two types of potential loss, the top portion represents the loss to the air, calculated using $ML \times EF$. The bottom half of the diagram describes the total loss from the process based on simple liquid-phase mass balance, obtained by using $ML \times TLF$. The mass entering the next process $[ML \times (1 - TLF)]$ is presented below the vertical "down arrow" leaving the unit process.

Aerated Grit

In this plant, the total mass loading of toluene to the aerated grit chamber was calculated by multiplying the concentration by the liquid flow rate and the appropriate conversion factors, and determined to be 454 kg/yr (1000 lb/yr).

The air emission rate of toluene from the aerated grit chamber was determined by multiplying the total mass loading, 454 kg/yr (1000 lb/yr), by the emission factor, 0.0026 (kg/kg or lb/lb), from the PEEP final report. Using equation 1, the air emission is estimated to be 1.18 kg/yr (2.6 lb/yr).

The effluent concentration from the aerated grit chamber was estimated by subtracting the quantity of toluene lost in the process from the influent concentration. For this case, the
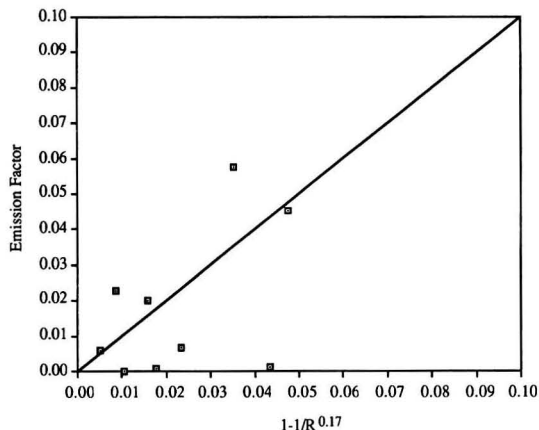

FIGURE 6. Correlation between *EF* and oxygen deficit ratio (air data at covered processes).

TLF is 0. A zero value means that there was no loss calculated across the chamber. This calculated value, 100 ppb, provides an estimate of the effluent liquid concentration from the grit chamber.

Primary Sedimentation Tanks

The inlet concentration to the sedimentation tank can be obtained from field sampling or using the *TLF*. The effluent concentration from the aerated grit chamber is essentially the influent concentration to the sedimentation tank, if there are no other liquid inlet streams. For multiple inlet streams, the total mass loading to the primary sedimentation tank can be determined by summing the mass loading from each stream.

The procedures described above for the aerated grit chamber are repeated for the sedimentation tank. Using the same liquid flow rate and a 100 ppb concentration, the mass loading to the sedimentation tank was calculated to be 454 kg/yr (1,000 lb/yr). The toluene emission from the sedimentation tank was 3.9 lb/yr with an *EF* value of 0.0039. At a *TLF* of 0.15, the primary sedimentation tank effluent mass loading was calculated to be 386 kg/yr (850 lb/yr). This loading represents the mass loading to the activated sludge process.

Remaining Processes

Similar procedures were then applied to the rest of the process train. The methodology for estimating the air emissions from the backwash operation of tertiary filters is the same, that is, $ML \times EF$. However, the liquid concentration of inlet backwash water should be determined via sampling or other appropriate methods. In addition, the actual flow rate of the backwash water should be used, rather than the total filtered flow.

If the effluent liquid toluene concentration from the diffused air activated sludge basin is non-detectable in the sample, then, it is not necessary to proceed with emissions estimates for subsequent processes. For the purpose of illustration, the field samples for the "typical" POTW from the effluents of the aeration basins and secondary clarifiers were assumed to contain 5 and 4 ppb toluene, respectively.

Model Recalibration

The *TLF*s from the diffused air activated sludge and secondary clarifiers are both 1.0. The 1.0 value means that the

effluent toluene concentration from these processes is either below the detection limit or at zero. It is suggested that samples be collected from the effluent liquid streams of these processes to recalibrate the estimation process.

Air Emission Estimate for Solid/Gas Handling Systems

The estimating procedures for air emissions from solid and gas treatment processes are similar to those used for the liquid stream and are shown in Figure 8. In this example plant, it was assumed that the flow rate to the gravity thickener unit was 2,500 m³/day (0.66 mgd) with a toluene concentration of 20 ppb. The mass loading was calculated as 18.2 kg/yr (40 lb/yr). With an emission factor of 0.051, the calculated emission of toluene from the gravity thickener is 0.91 kg/yr (2.0 lb/yr).

From the thickener, the liquid stream was returned to the liquid process train and the solid/sludge stream was fed to the anaerobic digester. If the liquid flow rate in the treatment train is assumed constant (as in this example), the emission from this returned liquid stream would have already been included in the estimate from the liquid treatment train. Consequently, it is not necessary to estimate the emission from this stream separately. The toluene concentration of the returned liquid stream could be estimated using the TLF, −0.055. Since the calculated effluent concentration, 21.1 ppb, was higher than the influent concentration, field samples should be analyzed to recalibrate the model.

The TLFs in the PEEP report do not provide a direct estimation method for the concentrations in the solid stream. Instead of using the calculated concentrations of the effluent liquid stream as a rough estimate, a more accurate solid concentration could be obtained from field sampling. Judicious use of the PEEP factors and selected field samples should provide reasonable emission estimates.

By assuming a sludge flow rate of 493 m³/day (0.13 mgd) to the anaerobic digester and a toluene concentration of 30 ppb (a recalibrated value), the mass loading to the digester is 5.4 kg/yr (12 lb/yr). The digester has an EF value of 2.1, therefore, the air emission of the toluene from the digester is 11.4 kg/yr (25.2 lb/yr). Using a TLF of 0.54, the toluene concentration in the digested sludge was calculated to be 13.8 ppb. Accordingly, the toluene mass loading to the belt press was 2.5 kg/yr (5.5 lb/yr). With an emission factor of 0.45, the toluene emission from the belt press was calculated to be 1.1 kg/yr (2.5 lb/yr).

IC Engines and Boilers

The emission rate of combustion processes such as digester gas-fired IC engines and boilers, can be determined using similar methodology. In this approach, the emission rate from a specific combustion unit can be determined from the EF values and percentage of total plant digester gas used by the unit.

This value could be used as a basis for estimating emissions from the gas treatment processes. It should be noted here that the EF value of toluene is greater than unity. It implies that toluene may be produced as a byproduct in the digestion process.

If 20% of the total digester gas was in the IC engines in one year, then, 2.3 kg (5.0 lbs) of toluene were loaded to the IC engines that year. By applying an EF value of 0.58 (kg/kg) for engines without NOx control, the estimated emission rate is 1.4 kg/yr (3.0 lb/yr). The derived EF value is based on total mass loading including potential contributions from the ambient air.

Overall POTW Air Emissions

For this example plant, the total toluene emission was 165 lb/yr, which represents approximately 16.5% of the total mass loading to the liquid treatment train. Emissions from the aeration basins (61.2 kg/yr [136 lb/yr]) account for 82.5% of the total emission (75 kg/yr [165 lb/yr]).

CONCLUSIONS

There are several competing mechanisms for removal of organic compounds in wastewater treatment plants, sorption onto solids/biomass, volatilization, biodegradation, and chemical oxidation [12–18]. The extent of volatilization is interrelated with the removal mechanisms. Therefore, physicochemical parameters will impact both the extent of substance removal and the potential for air emissions from POTWs. These parameters include:

- surfactant content;
- oil and grease content;
- biodegradation rate;
- biomass concentration;
- operating parameters, such as aeration rate and residence time;
- environmental conditions, such as temperature and wind speed; and
- characteristics of the compounds, such as Henry's constant, biodegradability, diffusivity, and adsorption coefficient.

The transport and fate of organic chemicals involves a complex interaction of these parameters. Such interactions are not easily modeled. Recent efforts indicate wide differences in percentages of organic components estimated to follow the various fate paths. For example, volatility (Henry's constant) is expected to have a large impact on fate predictions, and is one of the most often studied properties. However, for important volatile organic compounds, Henry's constant values located in the literature can differ by more than 50% [19–22]. Investigations into other parameters and models indicate similar disparities. It is plausible to say only that the extent of air emission for each unit process is controlled by a complicated network of removal mechanisms, but the current state of knowledge does not provide sufficient guidance for reasonable estimation of air emissions.

The EFs developed in PEEP, are based on rigorous field sampling methodology and analytical data. EFs backed by this substantial data base provide more accountable estimates of air emissions than those available in the literature. The PEEP project is one of only a few studies which include air emission from the solid/sludge handling processes at POTWs. As concerns about air emissions from wastewater treatment plants are increasing, more studies of this nature are warranted to confirm the PEEP results, to extend the studies to other waste streams with higher concentrations and various compounds, and to incorporate more operating parameters. The number of compounds detected in the liquid and air streams during PEEP testing are smaller than previously thought. Consequently, studies on upstream release become a more important focus.

In summary, the culmination of the PEEP effort is a POTW-specific mechanism to estimate air emissions. Utilizing a small amount of operational data and the PEEP emission factors, one can estimate air emissions on a process-by-process basis in a series of simple calculation steps. This method produces a more accurate estimate than that obtained using a simple liquid-phase mass balance approach. An added benefit is that PEEP EFs can also be used to perform sensitivity analyses for capacity increases, process changes and changes in wastewater composition. For example, the impact of a 50% reduction in influent VOCs due to a modification in an industrial pretreatment program on the total air emissions could be estimated using the PEEP EF values. The current plan of PEEP PAs is to make the final report available to the general public by the end of 1991.

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The Quality Improvement Program (QIP): A New Regulatory Strategy for Sustaining Long Term Reductions in Emissions from Equipment Leaks

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During the remainder of this decade and into the next century, chemical and refining industries will have an unprecedented opportunity to work closely with equipment suppliers, process engineering and construction firms, maintenance personnel, regulators, and the community to improve their environmental performance while enhancing the operation of their facilities. The basis of the strategy for this change will be the new Clean Air Act, which was passed into law in November 1990. The impetus for improvement will be the Quality Improvement Program (QIP) for controlling fugitive emissions from equipment leaks. Although results from the QIP need not be incorporated into the technology of an operating chemical plant or refinery until 1999, best results can be achieved by analyzing monitoring and maintenance information obtained in the early phases of fugitive emissions activity as soon as possible, and utilizing this analysis in evaluating technology and selecting new process design configurations.

INTRODUCTION

In November 1992, EPA proposed five new MACT (Maximum Achievable Control Technology) Standards under Title III of the New Clean Air Act for the following emission source categories (see Figure 1):

- Storage Tanks
- Process Vents
- Wastewater Treatment Operations
- Transfer Operations
- Equipment Leaks

While each of these standards focuses on a different aspect of the chemical plant, together they cover all major air emission points within a typical facility. To varying degrees, each of these is based upon a similar regulation (NSPS, NESHAP, RCRA) already in place. However, the standard for controlling emissions from equipment leaks includes a truly unique provision known as a Quality Improvement Program (QIP). This provision makes this rule different from most existing environmental regulations in that its purpose is not to penalize a

unit that is unable to comply with limits set under the rule, but rather, to generate information that can serve as the technical basis to bring the unit into compliance. This would be done through the use of quality principles stressing continuous improvement.

The concepts in the Quality Improvement Program were first proposed by industry during the regulatory negotiation process as indicative of the kinds of programs being successfully implemented in other operating areas, and representative of the kind of a regulatory program which could provide a positive basis for continuous improvement of noncompliant facilities. These were adapted by the EPA and adopted by the committee. Before outlining the details of the Quality Improvement Program, it is important to recognize the historical issues associated with fugitive emissions from equipment leaks.

FUGITIVE EMISSIONS

Fugitive emissions are low-level diffuse volatile organic compound emissions that occur when process fluid (either gaseous
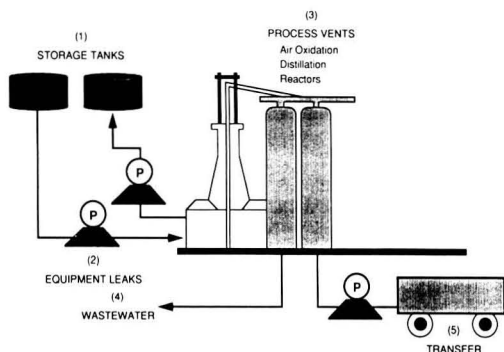
FIGURE 1. Affected source types for MACT. Source: USEPA

or liquid) escapes from plant equipment such as valves, flanges, pumps and compressors, into the atmosphere. As a class, such compounds are believed to be precursors in the formation of tropospheric ozone or smog in urban areas and will be addressed under Title I of the new Clean Air Act. Some specific chemicals are of a sufficiently high level of additional concern because of their toxicity, explosivity or flammability to warrant also being addressed under the Hazardous Air Pollution provisions of Title III. The U.S. Environmental Protection Agency (EPA) has noted that in the 1988 Toxic Release Inventory (TRI) about 40 percent of reported air emissions from a typical chemical plant were from fugitive sources. EPA also warns that these generally ground-level emissions have a potential impact on the nearby community that is 10 to 40 times greater than that from comparable emissions from elevated sources. These emissions are unlike any other environmental concern within a chemical plant or industrial complex because they occur, not from one easily measured and monitored source but from thousands of diffuse sources, which represent the very heart of the petrochemical process. The function of these sources is easily understood by any unit operator or technician. Yet, because fugitive emissions are only symptoms of some more fundamental problem associated with the component design and operation, even the most experienced operations manager or design engineer may not understand the multitude of factors that result in leaks.

Clearly, in developing rules for the new Clean Air Act, fugitive emissions were believed to be a category of emissions that warrant specific attention. But, other problems associated with fugitive emissions that can adversely affect a chemical plant's performance, and would already warrant special attention and correction in a fugitive emissions reduction program include [1]:

- Safety: Explosions and fires
- Health: Operator and community exposure
- Reliability: Equipment failure and unit shutdown
- Regulatory: Compliance
- Community Image: Corporate proactiveness
- Economic: Product loss

Several of these concerns are addressed in Title I (Nonattainment) and Title V (permitting) under the Clean Air Act, or under the accidental release provision of Title III. Unless all of these concerns are integrated into a total fugitive emissions control program, a unit might jeopardize long-term reliability (which could lead to explosions, exposure or fires) by using unsafe or unproven technology to achieve short-term reductions in fugitive emissions.

The magnitude of the problem being faced by the chemical and refining industry in addressing the question of fugitive emissions from equipment leaks was recently illustrated by

NASA's frustration when it attempted to find and eliminate hydrogen leaks within the space shuttles Columbia and Atlantis [2]. Despite having virtually unlimited resources at its disposal, NASA failed to rapidly find and eliminate these leaks, which led to a number of launch cancellations, and a complete reevaluation of the space shuttle's program's viability. In this case, the problem was not focused on product loss or community exposure but on fires, explosions and operator safety, which are also major concerns within a chemical complex and petroleum refinery.

BACKGROUND

While the chemical and refining industries have always been concerned over fugitive emissions from equipment leaks, the focus of control efforts began to change during the last two decades. After a series of studies at a number of refineries and chemical plants, EPA concluded in the late seventies that fugitive emissions from these sources can be significant. In those cases where fugitive emissions may need to be controlled, the Agency developed a special monitoring procedure which simplified emissions measurement (The Leak Detection and Repair Program—LDAR). By using a standard Organic Vapor Analyser, an operator could determine if the component was a leaker (screening value above 10,000 ppm) needing repair or a nonleaker which was acceptable. No additional effort was needed, except that records of the monitoring and repair activities had to be kept. Based upon the EPA's studies, it was concluded that a large portion of the emissions from a refinery or chemical plant were from the leakers.

After many individual companies began collecting fugitive emissions data that indicated that their emissions were much lower than had been estimated from EPA factors, in late 1987, producers of phosgene, butadiene, acrolein and ethylene oxide approached EPA and suggested that they jointly conduct a series of monitoring studies to better define fugitive emissions. The belief was that because of concerns over fires, explosions, and operator and community exposure, emissions from these industries would be much lower than had been indicated by the average factors previously developed. Overall, 39 chemical plants participated in these studies, including all domestic producers of ethylene oxide, phosgene and acrolein. Between 1988 and 1990, nearly 100,000 components were screened with the Organic Vapor Analyzer, and an additional thousand specific components bagged [3, 4].

Overall, results of the industry-wide screening and bagging studies were revealing to all participants (Figure 2). The percentage of leakers (> 10,000 ppm) found in these studies was markedly below that previously found in the EPA's studies, with major differences between the four industries also ob-
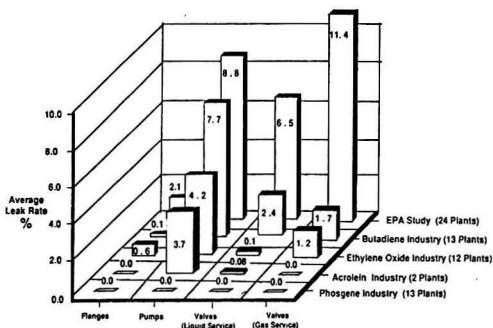

FIGURE 2. Comparison of leak frequencies for critical components in acrolein, butadiene, ethylene oxide, and phosgene industries relative to the original EPA studies.

served. Furthermore, 99.8 percent of the components in the phosgene unit, 98.6 percent of the components in the acrolein units, 86 percent of the components in an ethylene oxide unit, and 75 percent of the components in a butadiene unit had screening values that were below the level of detection of the monitoring instrument (about 10 ppm for acrolein, butadiene and ethylene oxide on the OVA, 0.2 ppm for phosgene with a specific phosgene analyser), indicating that low leakage can be achieved. Understanding the reason for difference in leakage is fundamental to developing an understanding of fugitive emissions and an effective control strategy. But, the reasons being proposed to explain these differences by each unit in isolation, were often based upon ignorance, intuition or imagination. Thus, a special survey was prepared and distributed to all participants in these studies. The first part of this survey addressed operational characteristics of production facilities (nature of chemical, temperature, pressure, surges, etc). The second part of the survey was focused on three fundamental aspects of fugitive emissions control: (1) programs for leak monitoring, (2) practices for maintaining a component or repairing the leak once detected, and (3) procedures for preventing the occurrence of a leak through special design standards. The aggregation of responses to these survey questions presented striking corrections to prior conceptions.

The survey results indicated that there were variations between industries (and within individual units) with respect to volatility, corrosivity, acute toxicity, and molecular properties of the chemicals of concern and the operating pressure, temperatures, and cycles of the different operations, all of which could have some impact on the ultimate fugitive emission levels achievable in these units. But, these operational characteristics did not appear to be the most important factor controlling fugitive emissions leakage. Neither did the presence of a mandated leak detection and repair program assure low fugitive emissions. Rather, the measured fugitive emissions levels appeared to have been achieved as an indirect consequence of the different industries' existing internal and external programs for safety, employee health, exposure, and environmental control.

The benchmark facilities—the producers of acrolein, phosgene, and in many cases, ethylene oxide, apparently recognizing the potentially acute health hazards of these chemicals, seem to operate from a strategic plan that assures low fugitive emissions from components that handled these chemicals. The overriding strategy was simply that equipment leaks were not tolerated.

For years these industries had initiated special procedures to reduce leaks in the areas of maintenance, monitoring, and design. These included the following:

• Monitoring: In the benchmark plants, the staff is trained to be sensitive to leaks and operators are constantly looking for leaks.
• Maintenance: Leaks are appropriately repaired; when necessary, the unit is shut down.
• Design: Units are designed to minimize leakage, to allow rapid shutdown and startup, and to minimize the number of components. A leakless design is focused on three critical areas:

1) difficult-to-maintain locations,
2) components on streams requiring excessive maintenance, or
3) components with severe consequences should they begin to leak.

It is important to recognize that many units cannot be operated as indicated above. Although phosgene and acrolein units are often shut down for maintenance on a quarterly basis, and ethylene oxide units are shut down annually, some large units have long operating cycles and cannot be easily shutdown without significant preparation. Furthermore, they may have more emissions in the shut-down/start-up cycle than would be eliminated by repairing a group of fugitive leaks. In other cases, some units, because of their size or operating characteristics cannot use much of the available leakless technology. Nevertheless, several key points can be made with respect to low leak performance in benchmark operations:

• No single maintenance, design, or monitoring method was used by all industries or even by most plants in any single industry. It was not a single silver bullet, but rather a set of ten commandments that was needed to achieve low fugitive emissions in benchmark units.
• Today's performance in benchmark units did not happen overnight; low fugitive emissions were the cumulative results of years of record keeping, analysis and effort.
• Low fugitive emissions were achieved primarily through use of conventional technology, not necessarily by universal application of new leakless technology.
• New technology was selectively used where it made good engineering sense.

The main theme that pervades the approaches used in benchmark industries to assure low fugitive emissions is that while advanced technology may be adopted, low levels of fugitive emissions result from paying attention to details of the operation and responding appropriately to any leakage regardless of size. To assure low fugitive emissions, the operating staff must be interested in actually reducing fugitive emissions, not just in meeting a fugitive emissions rule.

REGULATORY DEVELOPMENT

Regulators have been looking at equipment leaks as a source of emissions to the environment since the early 1950's. Initial efforts at controlling fugitive emissions focused on reducing these releases in ozone nonattainment areas as an effort to reduce production of smog. Thus, fugitive emissions were required to be addressed in State Implementation Plans (SIPs) for some areas. Furthermore, since the late 1970's, all new production units needed to have a fugitive emission control program in place (following the New Source Performance Standard). With the passage of vinyl chloride and benzene NEHSAPS (National Emission Standard for Hazardous Air Pollutants) under the 1970 Clean Air Act, concerns with fugitive emissions of hazardous air pollutants were also addressed.

All of these approaches followed a similar procedure.

1) The rule applied to components on a stream containing more than a minimum amount of the chemical of concern (i.e., >10%).
2) The equipment of concern (valve, pump, compressor, etc.) was monitored on some regular basis. This varied from once per month to once per year.
3) If equipment was "leaking," (i.e., screening value above 10,000 ppm) it was to be repaired within a prescribed period (generally 5 to 15 days unless a delay was warranted).
4) If equipment was not "leaking" (i.e., screening value below 10,000 ppm), it was ignored.
5) To estimate emissions from a piece of leaking equipment, the approved "leaking" factors were used. To estimate emissions from a non-leaking piece of equipment, a special "non-leaking" factor was used. Overall, the nonleaking factor was still quite large.
6) Units that had extensive internal programs to eliminate fugitive leaks and were finding that they had no "leaking" components were still having to report emissions that were quite substantial.
7) Units that used leakless technology would not be required to monitor components on a regular basis.

In essence the EPA Leak Detection and Repair program focused attention on finding and fixing a leak rather than preventing it.
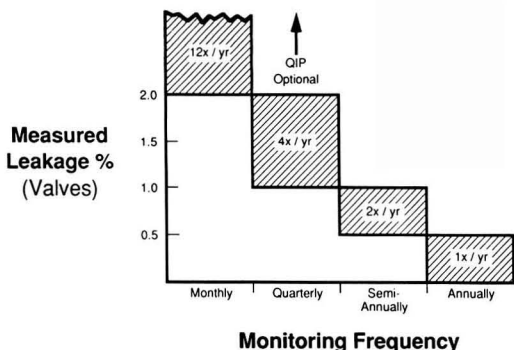
FIGURE 3. Valves—relationship of measured leak rate to allowed monitoring frequency.

REGULATORY NEGOTIATIONS

Following the industry-wide fugitive emissions studies for acrolein, butadiene, ethylene oxide and phosgene industries, it was generally recognized that these industries did indeed have lower fugitive emissions than had been observed in earlier studies. But, it appeared from the surveys and data analysis, that the low levels of fugitive emissions reported in some of these industries could be achievable by any process unit making a commitment to eliminate these leaks.

Accordingly, when the need for new fugitive emissions regulation was being evaluated, a special regulatory negotiation committee was formed to develop the new fugitive emissions rules. Participating in this committee were representatives of the chemical, oil, pharmaceutical, and rubber industries, state, local and federal regulators, and environmentalists. After nine months of technical presentations, data analysis, and negotiations, consensus was achieved on a new rule which appeared to incorporate the best of the old fugitive emissions rule with insights gained from the new studies [5].

This rule had the following attributes:

1) It would reduce concentration of streams included in the rule from above 10 percent to above 5 percent.
2) It would replace existing leak definition (10,000 ppm) with a lower leak definition (500 ppm).
3) It would replace the fixed monitoring period of once per quarter with a flexible monitoring period which would vary depending upon the leakage found in the unit. For example, if less than 0.5% of the valves leaked, the monitoring frequency could be decreased to once per year. But, if more than 2% of the valves leaked, monitoring frequency would have to be increased to once per month (See Figure 3 for valves).
4) It would establish a maximum allowable leak limit (e.g., 2% for valves), which when exceeded, would require the unit to begin to gather more data on the components in the unit which can ultimately be used to modify overall design of the unit, or design of individual components in the unit. All valves would be monitored (including leakless technology) and used in determining a leak rate.
5) It would provide a long period of time (6 years or more) for the unit to get into the program. While some units (olefins, ethylene) have long operating cycles which may allow only one shutdown, most units should have several chances to install and test new equipment.
6) It would require comprehensive data gathering, analysis, interpretation and testing. Use of industry consortiums would be encouraged.
7) It would not require that all chemical plants or refineries implement the rule at the same time. Chemical operations would be placed into five groups. Each group would have a different effective date for the rule (varying in 3 month in-

crements over a year), beginning 6 months after the rule is promulgated. Refineries would be handled in a separate rulemaking effort.

The new rule was proposed in November 1992 and would be implemented in three phases (Figure 4):

Under the expected schedule for the operations handling the first group of chemicals (Group I), Phase I would begin around June 1994 (6 months after promulgation). It would basically follow the pattern of existing fugitive emissions NSPS and NESHAPS. It would maintain the leak definition at 10,000 ppm and have no leak limit. One year later, phase II of the rule would begin. The leak definition would be lowered to 500 ppm for valves (5,000 ppm for pumps), but there would still not be a leak limit. About 18 months later the third phase of the program would begin. In this phase, the lower leak definition of 500 ppm would be maintained for valves, while the leak definition for pumps would be reduced further to 1,000 ppm. But, a maximum leak limit would also be established (2% for valves, 10% for pumps).

Activity	Expected Date
Proposal	Nov. 1992
Promulgation	Nov. 1993
Phase I (Group I)*	June 1994
Phase II (Group I)	June 1995
Phase III (Group I)	Nov. 1996

*The implementation schedule for process units in Groups II, III, IV, and V increase by 3 month increments.

QUALITY IMPROVEMENT PROGRAM

If upon entering the third phase of the rule, a unit is exceeding the allowable leak limit, it will not be required to shut down; nor will it be fined or penalized. Rather, in the case of valves, it can either begin monthly monitoring, or enter one of two alternate quality improvement programs specified in the proposed rule (Figure 4). Under these two QIPs [6], a unit would be required to either:

1) *Demonstrate Further Progress*: Show a sustained reduction in the number of leaking components detected in the unit (10% per quarter). Or,
2) Begin the *Technology Review and Improvement* program.

The QIP programs are very similar for pumps and valves, except that pumps must move immediately to the Technology Review and Improvement QIP.

DEMONSTRATION OF FURTHER PROGRESS (DFP)

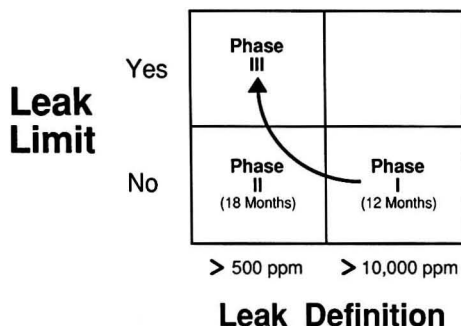To demonstrate further progress, information shall be col-

Leak Definition

FIGURE 4. Valves—comparison of three phases of rule with respect to leak definition and leak limit.

Table 1 Valves
Information to be Collected in Technology Review and Improvement QIP

Equipment
- valve type
- valve manufacturer
- valve design (external stem or actuating mechanism, flanged body)
- materials of construction
- packing material
- year installed

Service
- operating pressure
- temperature
- line diameter
- corrosivity
- gas or liquid service

Monitoring
- screening value
- instrument response value to stream
- date, etc.

Maintenance
- repair methods
- instrument readings after repair
- date of repair

Note: if appropriate, a description of any maintenance or quality assurance program used in the process unit that is intended to improve emission performance shall also be provided.

Inspection

Note: in addition, all valves removed from the process unit due to leaks shall be inspected. The inspection shall determine which parts of the valve have failed and shall include recommendations, as appropriate, for design changes or changes in specifications to reduce leak potential.

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lected and records maintained for each valve subject to the QIP. This information would be collected in the following areas:

Monitoring

- the maximum instrument reading observed during screening
- the response factor for the stream, if appropriate
- the instrument model number
- the date of the observation

Process

- for a valve, whether it is in gas or liquid service.

Maintenance

- if a leak is detected, repair methods used and instrument readings after repair.

Successfully demonstrating further progress shall mean that for each quarter there should be at least a 10% reduction in the percent of leaking valves from the preceding monitoring period (using a 2-month rolling average). If, for 2 consecutive

quarters at least a 10% reduction per quarter in percent leaking valves is not achieved the unit has not successfully demonstrated further progress in reducing its fugitive emissions. It will need to either begin monthly monitoring, or agree to adopt the QIP for Technology Review and Improvement (TRI).

TECHNOLOGY REVIEW AND IMPROVEMENT (TRI)

In the Technology Review and Improvement QIP, more information will need to be collected. This information is summarized in Table 1 for valves and Table 2 for pumps.

ANALYSIS

The above information shall be analyzed to determine services, operating or maintenance practices and valve or pump designs or technologies that have poorer than average emission performance and those that have better than average emissions performance. The analysis shall determine if specific trouble areas can be identified on the basis of service, operating conditions or maintenance practices, equipment design, or other process specific factors.

Table 2 Pumps
Information to be Collected in Technology Review and Improvement QIP

Equipment
- pump type (e.g., piston, horizontal or vertical centrifugal, etc)
- pump manufacturer
- pump design (e.g., external shaft, flanged body)
- materials of construction
- barrier fluid, if applicable
- packaging material
- year installed

Service
- discharge pressure
- temperature
- flow rate
- corrosivity
- annual operating hours

Monitoring
- screening value
- instrument response value to stream
- date etc.

Maintenance
- repair methods
- instrument readings after repair
- date of repair

Note: if appropriate, a description of any maintenance or quality assurance program used in the process unit that is intended to improve emission performance shall also be provided.

Inspection

Note: all pumps or pump seals which exhibited frequent seal failures and were removed from the process unit due to leaks shall be inspected. The inspection shall determine the probable cause of the pump seal failure or of the pump leak and shall include recommendations, as appropriate, for design changes or changes in specifications to reduce leak potential.

SUPERIOR PERFORMING TECHNOLOGIES

The analysis shall also be used to identify any superior performing technologies that are applicable to services, operating conditions, or designs associated with poorer than average emission performance. A candidate superior performing technology is one for which a group of such equipment demonstrated or reported as being capable of achieving less than 2% leaking valves or less than 10% leaking pumps in the process unit.

The analysis shall include consideration of:

- Inspection data from valves or pumps removed from the process unit
- Information from the literature
- Experiences from other plant sites
- Information on limitations on service conditions for the equipment design and operating conditions as well as information on maintenance procedures to ensure continued low emission performance

The first analysis of data collected in the QIP program shall be completed no later than 18 months after the start of Phase III. The first analysis shall be performed using a minimum of 2 quarters of data. A further analysis of the data shall be done annually for as long as the process unit is in the QIP.

TRIAL EVALUATION

A trial evaluation program shall be conducted at each plant site for which data analysis does not identify superior performing designs or technologies that can be applied to operating conditions and services identified as having poorer than average performance. The number of valves in the trial program shall be the lesser of 1% or 20 valves (or 1% or 3 pumps) for single process units (1% or 50 valves for groups of process units). This program shall be used to evaluate the feasibility of using, in the process unit, the valve or pump designs or technologies that have been identified by others as having low emission performance.

The trial program will include

1) on-line trials of specific valve or pump types or manufacturers
2) operating and maintenances practices believed to have:
   the ability to achieve leak rates below 2% in similar services (below 10% for pumps)
   a low probability of failure
   no external actuating mechanism in contact with process fluid

If a candidate superior performing technology is not included in the performance trials, reasons for rejecting specific technologies from consideration shall be documented.

The trial evaluation program shall specify and include documentation of:

- The candidate superior performing designs or technologies to be evaluated, stages for evaluating the identified candidate designs or technologies, including the estimated time period necessary to test applicability of the technology.
- The frequency of monitoring or equipment inspection.
- The range of operating conditions over which the equipment will be evaluated.
- Conclusions regarding emission performance and the appropriate operating conditions and services for the trial equipment.

Performance trials shall initially be conducted for at least a 6-month period beginning not later than 18 months after the start of Phase III. Not later than 24 months after the start of Phase III, designs or technologies shall be identified that, com-

bined with appropriate process, operating and maintenance practices, can achieve low emission performance for specific applications in the process unit. Performance trials shall continue to be conducted as long as no superior performing design or technology has been identified. If a superior performing design for this application is not identified, performance trials can be discontinued, but an engineering evaluation must be undertaken. This evaluation must document the physical, chemical, or engineering basis for the judgement that the superior emission performance technology is technically unfeasible or demonstrate that it would not reduce emissions.

QUALITY ASSURANCE PROGRAM

If the QIP for technology review and improvement is adopted, a quality assurance program shall also be prepared and implemented that details purchasing specifications and maintenance procedures for all valves or pumps in the process unit. Different specifications and procedures may be established for any number of categories, or classes of valves or pumps as needed to distinguish among operating conditions and services associated with poorer than average performances. This Quality Assurance Program shall be reviewed and updated

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Table 3 Documentation Reports Needed for Fugitive Emissions Rule and Quality Improvement Program

1. Initial Fugitive Emissions Report
   When initiating program
   Identify process unit and equipment under the rule and the planned monitoring schedule

2. Semiannual Fugitive Emissions Report
   6 months after initiating program
   Summarize leaking/nonleaking components
   Report leaking frequency
   Outline repair attempts and progress
   Address modifications to initial report
   Notify of initiation of QIP, monthly monitoring, etc.

3. Quality Improvement Program Analysis
   18 months after initiating QIP and annually thereafter
   Summarize the analysis of the data collected in the QIP program

4. Trial Evaluation Program
   18 months after initiating QIP
   Document technologies to be evaluated, operating conditions, monitoring/inspection frequency, etc., for trial evaluation

5. Superior Emissions Performance Technology
   6 months after initiating trial evaluation and as appropriate thereafter
   Document physical, chemical, engineering basis for the judgement that the superior emission performance technology is technically infeasible

6. Quality Assurance Program
   24 months after initiating QIP
   Purchasing specifications
   Design standards
   Bench testing procedures

7. Off-line Maintenance and Repair Procedures
   24 months after initiating QIP

8. Audit Procedure to Assure Quality Control of Purchased Equipment
   24 months after initiating QIP

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each year as long as the process unit has 2% or more leaking valves (or ten % or more leaking pumps). The Quality Assurance Program shall also:

- Establish minimum design standards for each category of equipment. The design standards shall specify known critical parameters such as tolerance, manufacturer, materials of construction, previous usage, or other applicable identified critical parameters;
- Require that all equipment orders specify the design standard (or minimum tolerances);
- Include a written procedure for bench testing of valves that specifies performance criteria for acceptance of valves and specifies criteria for the precision and accuracy of the test apparatus. All valves repaired off-line after development of the quality assurance plan shall be bench tested for leaks.

The bench testing may be conducted by the process unit staff, the vendor, or a designated representative. Only those valves that have been documented through bench testing to be nonleaking (capable of achieving low-leak performance) shall be installed in the process unit.

REPAIR AND REPLACEMENT

Valves repaired on-line shall be re-monitored for leaks for 2 successive months after repair.

Off-line valve or pump maintenance and repair procedures shall be documented. These procedures shall include provisions to ensure that rebuilt or refurbished valves or pumps will meet design specifications and will operate such that emissions are minimized. Valves or pumps shall be maintained as specified in the QAP.

At the start of the third year of phase III, each valve that is replaced for any reason shall be replaced with a new or modified valve that meets quality assurance standards of the valve category that is identified as superior emission performance technology. Twenty percent of pumps shall be replaced

annually with superior emission performance technology (but, this can be postponed until the next shutdown).

Superior emission performance technology means valves or valve technologies identified with emission performance such
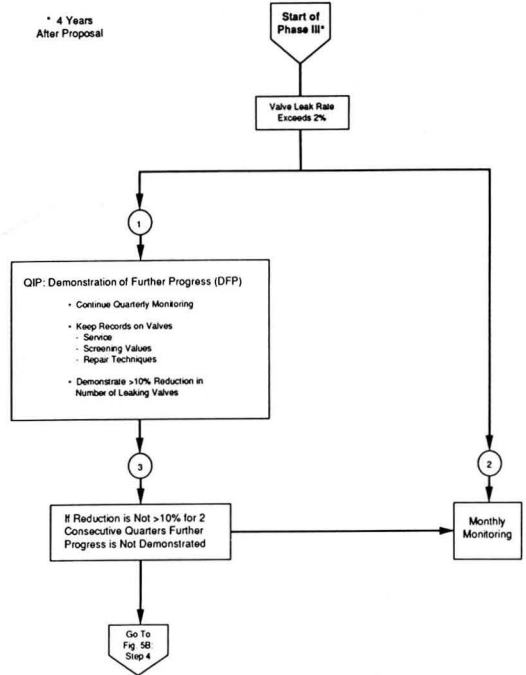
FIGURE 5A. Summary of quality improvement program for reducing emissions from equipment leaks: valves only segment.

FIGURE 5. Summary of quality improvement program.
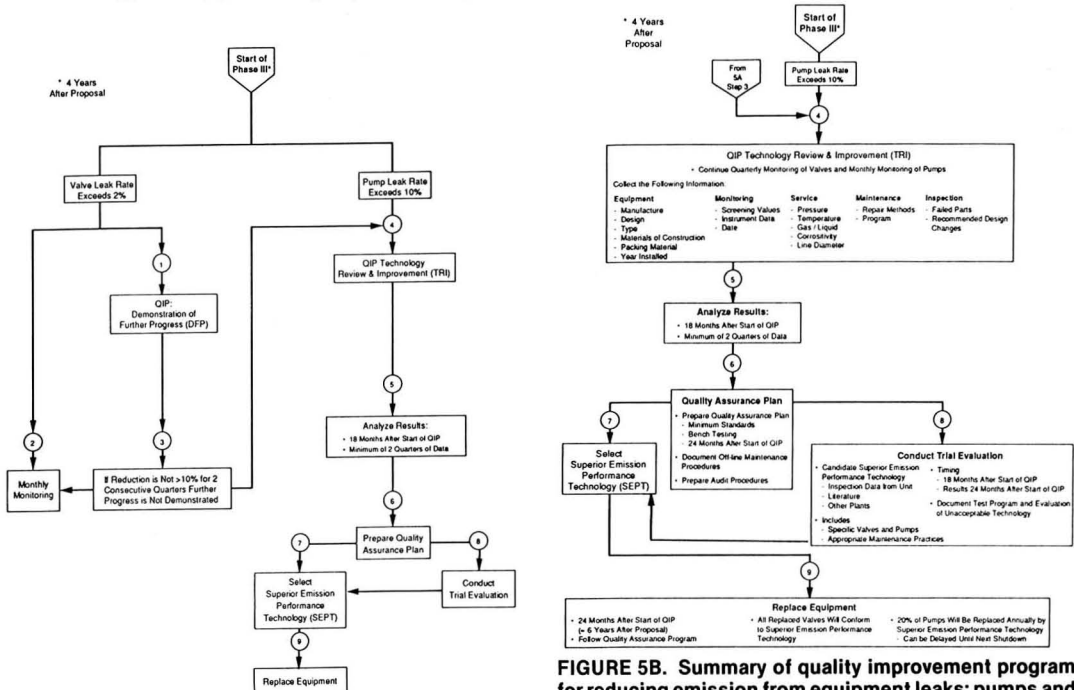
FIGURE 5B. Summary of quality improvement program for reducing emission from equipment leaks: pumps and valves segment.

Table 4 Ten Commandments for Controlling Emissions From Equipment Leaks Following the QIP

1. Constantly look for leaks.
2. Repair leaks with a priority.
3. Unsafe, unproven, or exotic technology shall not be required.
4. Improved design technology may not be necessary in most applications, but quality equipment will be demanded.
5. Improved design technology may not be sufficient in many applications.
6. Monitoring, maintenance and design activities must be integrated.
7. Detailed records shall be kept.
8. Comprehensive information analysis is required.
9. Performance trials of equipment shall be required.
10. Instant results shall not be required, but continuous improvement is expected.

that, combined with appropriate process, operating and maintenance practices will result in less than 2% leaking valves for specific applications in a large population. If a superior emission performance technology cannot be identified, then valve replacement shall be with one of the lowest emission performance technologies that has been identified for the specific application. For pumps, superior emission performance technology includes material or design changes to existing pump, pump seal, seal support system, installation of multiple mechanical seals or equivalent, or pump replacement.

PROGRAM AUDITS

The unit shall provide for an audit procedure for quality control of purchased equipment to ensure conformance with purchase specifications. The audit program may be conducted by the operating staff or by a designated representative.

The Quality Assurance program shall start not later than the third year of phase III, (a year later for smaller plant sites).

SUMMARY

Fugitive emissions can be successfully controlled by following the approach outlined in the new Quality Improvement Program. The QIP program will require that a large amount of performance data be gathered from valves in a regulated production facility, and a significant number of reports prepared. This data will be used to help that unit, and indirectly other units, select the best performing valve technology, that ultimately will help lower fugitive emissions. An indirect value of this program is that the unit staff and corporate engineering department should be able to gain new insights on continuing performance of this equipment that should help increase long term reliability while enhancing overall environmental performance of the process unit.

There was no single solution to reducing emissions from equipment leaks. It requires a set of ten commandments. These are summarized in Table 4.

According to MACT being developed for Title III under the Clean Air Act, results of the Quality Improvement Program will not need to be implemented until 1999. However, other state or federal programs may require a faster schedule for obtaining results. Furthermore, as new equipment is being purchased, information being collected on present performance of the unit should assist in evaluating other key aspects of the QIP. As soon as this data begins to be collected, it should be recorded and used in the QIP.

New process units being conceptually designed and constructed between now and the year 2000 can achieve significant cost savings by using information from the QIP to: 1) select and install equipment capable of achieving superior emission performance and 2) develop and utilize special valve testing procedures and specific programs of preventative and predictive maintenance and replacement. There is nothing to be gained in delaying gathering of information needed in the fugitive emissions QIP.

Overall, developing a response to the QIP is a team effort. It must include representatives of operations, maintenance, purchasing and engineering and will require support from external contractors, equipment suppliers, and even competitors. Developing a program to respond to this complex effort is a challenge that will stress even the largest petroleum or petrochemical company.

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NOₓ Removal on a Coal-Fired Utility Boiler by Selective Non-Catalytic Reduction

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A plant for Selective Non-catalytic Reduction (SNR) of NOₓ emissions by NH₃ (ammonia) injection has been designed, installed and successfully tested on a 135 MWₑ coal-fired utility boiler. The final 2000 hours test was performed with the plant automatically controlled.

The NOₓ level in the untreated flue gas is typically 400–700 ppm, and NH₃ is injected at a molar ratio to NO between 0.6 and 1.8. Through most of the load range 50–70% reduction of the NOₓ emission was achieved.

The temperature window for the process is 850–1050°C, with an optimum at 950°C.

In order to minimize the emission of unburnt NH₃, natural gas was added in a molar ratio to NOₓ of about 1 in part of the load range. The plant met a demand of no more than 15 ppm NH₃ in the flue gas.

The research and development work needed for adoption of the SNR-process to coal-firing has been in progress through five years in a cooperation between Aalborg Ciserv International, The Technical University of Denmark, and the Danish power plant association ELSAM. The research program included basic laboratory research on the chemical kinetics of the process, pilot scale research on the reducing capacity and emissions of ammonia and urea, testing in laboratory scale and pilot scale of several additives for widening the temperature window and minimizing the NH₃ emission, and development of nozzles for good mixing of NH₃ into the flue gas.

The resulting concept is applicable for NOₓ-removal on several types of boilers.

INTRODUCTION

So far Selective Non-catalytic Reduction (SNR) of NOₓ has mostly been used for NOₓ control in oil-fired boilers having well-defined temperature conditions. The development goal for the AB-SNR-deNOₓ process was to make the SNR process fit for Danish utility boilers, fired with a large variety of coals of different origins. The real challenge in the development was to overcome the difficulties caused by the interactions between the narrow active temperature window of the reactions, the mixing of the gases, and the ever changing temperature profile in large scale boilers due to changes in load and coal type. After the 2000 hr final test period the AB-SNR-deNOₓ process

is now in commercial operation on a 135 MWₑ coal fired utility boiler and the theoretical and practical aspects of design and construction of new plants are available.

This paper describes the design and performance of the full scale plant as well as the research and development work carried out to reach the present level of knowledge.

THE CHEMISTRY

The overall reaction leading to NO reduction is [1]:

$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O$$
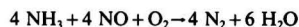
This reaction takes place in a temperature window around

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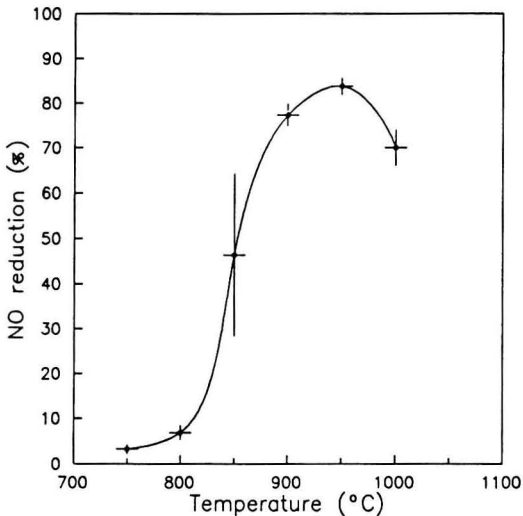
FIGURE 1. Temperature window for NO reduction by the SNR process as established in pilot plant experiments. Input flue gas is extracted from a large-scale boiler and contains about 500 ppm NO_x. NH_3 molar ratio to NO 1.6.

950°C [2, 3] (Figure 1). At higher temperatures the reduction of NO competes with oxidation of ammonia to NO by oxygen:

$$4 \, NH_3 + 5 \, O_2 \rightarrow 4 \, NO + 6 \, H_2O$$
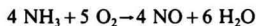
At too high temperatures, NH_3 will partially burn to NO without being made useful, whereas at too low temperatures unreacted NH_3 is emitted to the stack.

THE FULL-SCALE PLANT

The SNR-concept used during the final performance demonstration is illustrated in Figure 2. The 135 MW_e boiler gen-
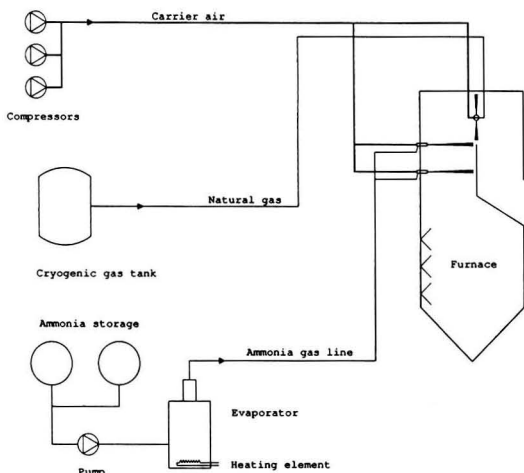
FIGURE 2. Principles of the full-scale SNR demonstration plant with NH_3 and natural gas additive (Boiler I, NEFO). As natural gas was not readily available on the site, liquefied gas was used during the test period.
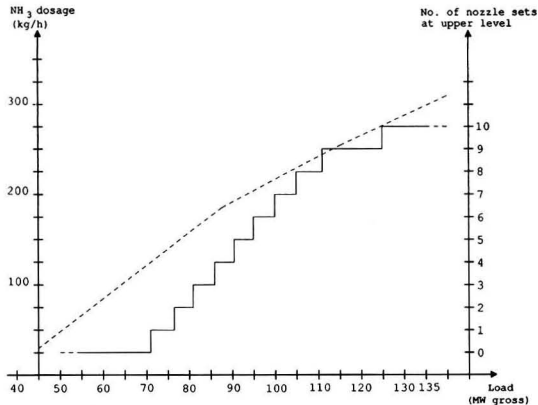
FIGURE 3. NH_3 dosage and injection point location versus boiler load. Dashed line: NH_3 in kg/hr. Step function: number of nozzle groups used at upper level.

erates between 55 and 120 Nm^3/sec of flue gas. The typical NO_x level is between 400 and 700 ppm.

To reduce this emission, NH_3 is evaporated and supplied to two nozzle levels, where it is mixed with carrier air before injection to the combustor. As reaction products between NH_3 and SO_2 represent a risk of fouling and corrosion in the coldest parts of the flue gas line [4], a limit of 15 ppm for NH_3 emission must be obeyed. In order to warrant this low NH_3 slip, natural gas may be injected through a separate nozzle level downstream of the ammonia injection. This feature is used in the upper half of the load range. When natural gas is used, more ammonia can be injected without exceeding the emission limit [5], and thus a higher NO_x reduction is secured.

NH_3 control is performed on the main line, but each nozzle is supplied with an individual shutoff valve. The control strategy includes a load-dependent distribution of NH_3 between the nozzle levels (see Figure 3). At any load the number of nozzles used is equivalent to one full level. But at increasing load (i.e., increasing furnace temperature) groups of injection points are successively moved from lower to upper nozzle level.

An NH_3 molar ratio to NO of 1.2–1.6 is normally used. At high loads however, when high temperature injection has to be used, the molar ratio may be raised to 1.8. Increasing the molar ratio up to about 2 still has a positive effect on the reduction, but at the cost of an increased NH_3 emission.

At low loads NH_3 is injected in the low end of the temperature window. This condition corresponds to a higher selectivity for the reducing process, but a lower reaction rate, so less NH_3 is consumed during the residence time in the boiler. In this case the molar ratio has to be small to avoid ammonia slip. In certain cases a molar ratio less than 1 has been used.

PERFORMANCE

During the 2000 hr period of final testing and documentation the SNR plant was in continuous, automatic operation, except for 2 or 3 daily half-hour periods, when the base NO_x level was established by turning off the NH_3 injection. By comparing the base level with the levels immediately before and after the shutdown periods, the relative reduction could be calculated. The results are depicted in Figure 4.

As shown, the NO_x reduction is between 50% and 70% in the load range 45 to 110 MW_e, and a little lower at full load. This performance might be improved by a third and perhaps a fourth nozzle level, the profit of which has to be weighed against the extra cost.
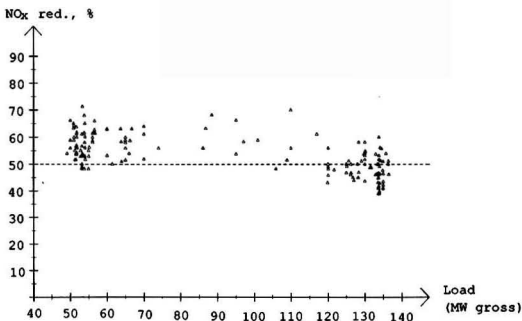
FIGURE 4. NOₓ reduction versus boiler load in the 2000 hr test period.

MAIN LINES OF RESEARCH

To reach the successful conclusion of the SNR project, research was carried out in several levels. Laboratory experiments gave a detailed knowledge of the process dependence on temperature, reaction time and reductant molar ratio. Also several additives have been tested in laboratory scale. A pilot-scale test rig was built in connection to a full-scale combustor, withdrawing flue gas from the main stream. On the pilot plant, a large number of additives were tested, and the two possible reductants ammonia and urea were compared.

A full-scale test plant was used for several test series at various development stages. This plant, which has been subject to major modifications according to research progress, is now going into commercial operation. Two mathematical models of the chemical processes were developed, including a detailed kinetic model based on elementary reactions, and a simple two-reaction empirical model. Finally, a boiler model, taking flow and mixing effects during the reducing process into account on an empirical base, was developed for design purposes and tested with good results.

LABORATORY FINDINGS

For the laboratory experiments a quartz flow reactor, designed for obtaining plug flow, was used. The central part of the reactor is shown as Figure 5. The reactor was used by Duo et al. [6, 7] and by Hulgaard et al. [8, 9]. The reaction tube (1) is cylindrical, 5.1 cm ∅, length 14 cm. The lower end of the reactor is connected to an air-cooled outlet tube (3). The main stream inlet (4) is used for the inert gases, primarily N_2, which are led through a preheating zone (2) before entering the reaction tube. Reactants are separately injected through inlet (5) and mixed with the main stream through the injectors (6) in the reaction tube.

The temperature window as established in the laboratory reactor is depicted in Figure 6 (from [6]). Note that Duo has chosen to depict the dimensionless outlet concentration of NO
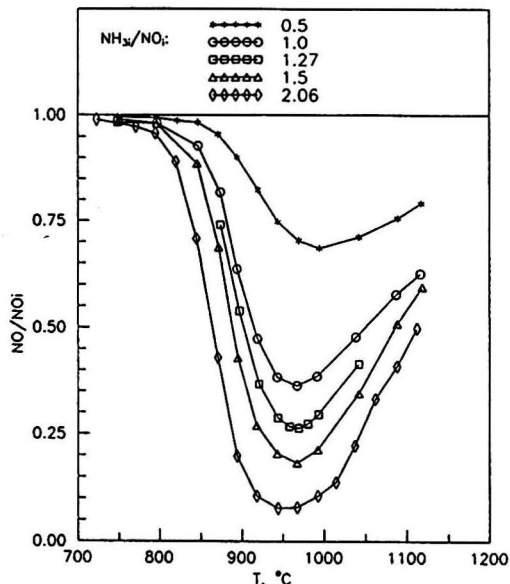
FIGURE 6. Dimensionless outlet temperature as observed in the laboratory reactor. Residence time 93.27 K·s/T [6].

instead of the degree of reduction, as preferred by the authors of this paper. The temperature window found in an isothermal bench-scale reactor on an artificial flue gas coincides very accurately with the window observed in the pilot-scale reactor with a temperature gradient of 200 K/sec, and with a coal-derived flue gas (Figure 1). Also the effect of several additives was tested in laboratory scale [6, 7].

PILOT-SCALE FINDINGS

Both gaseous ammonia and an urea solution [10] have been reported to be applicable as NO reductants, but a comparative test was still missing at the start of the present research project. As the laboratory reactor is only fit for gas injection, a versatile pilot-scale reactor, built in connection with the full-scale test plant as shown in Figure 7, was used for this test.

The reactor utilizes a flue gas stream of 400–700 kg/hr from the large-scale boiler. The gas is withdrawn through the five-section reactor by a fan mounted downstream of the pilot plant (at point B). The cooling rate is 200 K/sec, near to the conditions in a large-scale combustor. The end flanges provide easy access to any part of the channel for injecting gases or liquids, as well as for temperature and gas probes.

The reducing capacity did not distinguish the two reductants. When injected at the same NH_i/NO ratio, the reduction turned
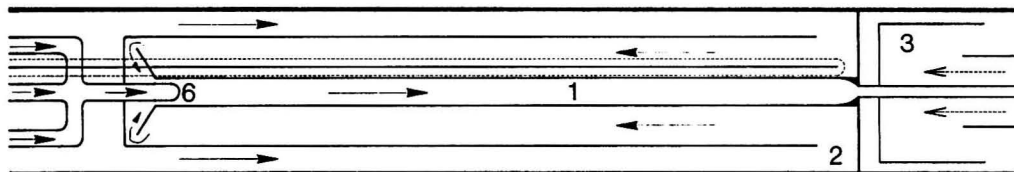
FIGURE 5. Central part of the laboratory flow reactor. The reactor is vertically mounted with flow direction downwards. 1: flow reactor, 2: preheating zone, 3: cooling zone; 4: main stream inlet, 5: reactant inlet, 6: micronozzle inserted in reactor [9].
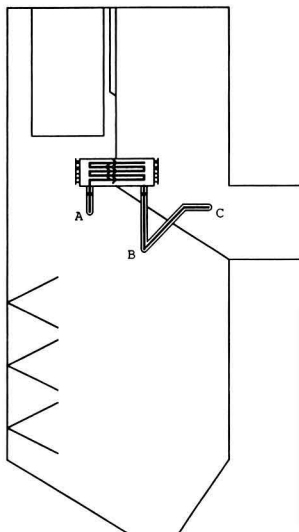
FIGURE 7. Pilot plant location on large scale boiler. A: Flue gas input (1100°C); B: gas control (slide gate and fan); C: exhaust gas output to main stream.

out to be almost identical, only the optimum with urea appeared at 1000° instead of the 950° found with NH_3.

Major difference was observed on the unwanted emissions. Figure 8 shows the NO_x reduction and the emissions of NH_3, CO, and N_2O (nitrous oxide) with both reductants. Note the large emission of N_2O with urea. As N_2O is a greenhouse gas, conversion of flue gas NO to N_2O must not be considered as denitrification. Note that urea shows an emission maximum only about 50° below the optimum reduction temperature. At this temperature the amount of nitrogen fixed as N_2O is well over half of what was originally found as NO. Also the emissions of CO and NH_3 are high at temperatures below 950°, when urea is used, so in practice only the upper half of the temperature window is viable.

These findings determined the choice of NH_3 as the reductant for the final concept. Also in the pilot plant several additives (hydrocarbons, alcohols, amines) were tested for their capability of broadening the temperature window. As the laboratory reactor was constructed for gases and volatile liquids, some liquid additives were tested in pilot-scale only. In other cases the additives were the same as in the laboratory test, thus allowing an evaluation of the effect of dust and trace elements in a real flue gas and of a temperature gradient. In most cases the effect of additives turned out to be similar in both scales.

Figure 9 shows the effect of propanol as an example. A number of additives were capable of improving NO_x reduction at low temperature. No additives capable of actually broadening the temperature window were found, but several species were able to move it. Based on the results obtained, natural gas was selected for full-scale additive testing.

Upscaling changed the effect of the additive considerably, as mixing effects turned out to be of major importance [11]. The resulting concept included injection of natural gas in the tail-end of the process through special nozzles.

NOZZLE DEVELOPMENT

In the original design of the SNR plant, the nozzle design was calculated by conventional fluid mechanics. The value of this calculation was disputed after the early test periods in full-scale, as NO_x reduction was found to be unexpectedly low,
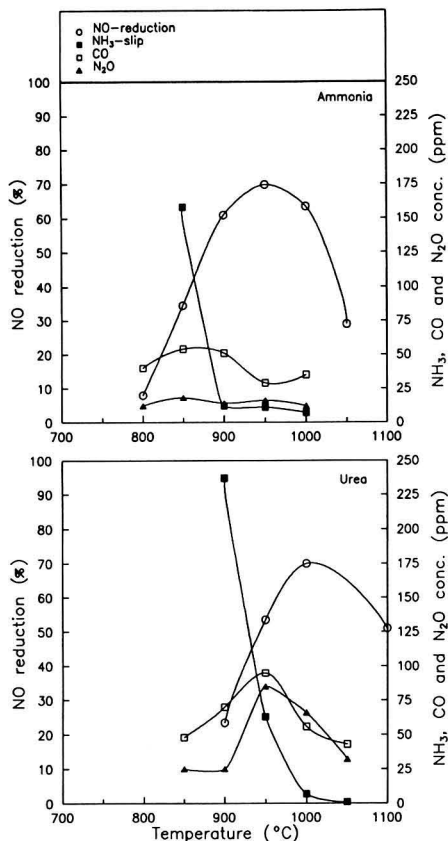
FIGURE 8. Reduction and emissions with either ammonia or urea as reductant. NH_i/NO molar ratio 1.3. NO level about 500 ppm [3, redrawn].
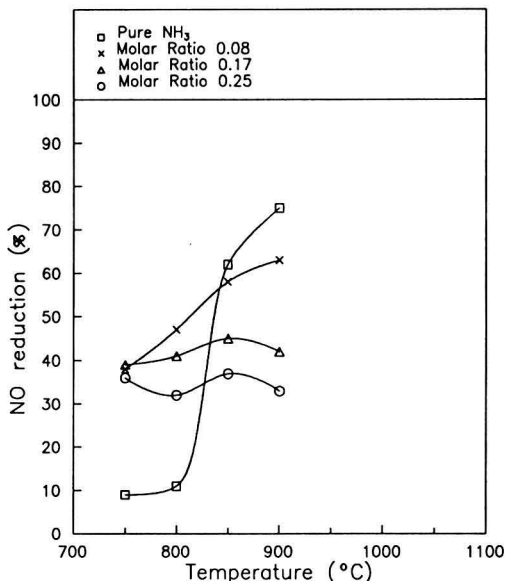
FIGURE 9. Reduction versus temperature, using the additive propanol. NH_3 is the primary reductant in a molar ratio to NO_x of 1.6.

especially at high load [12]. As this was attributed to insufficient mixing, a profound theoretical and empirical study of several nozzle types was carried out.

To aid the selection of nozzles for the next test period, three selected NH₃ nozzles were tested with a radioactive tracer in the hot boiler. The tracer test indicated very clearly, that the pre-estimated flow pattern was observed, even for the nozzle type with insufficient reduction.

The discrepancy between apparent distribution and observed performance must be interpreted as a result of interactions between chemical reactions and the mixing process. The main flow naturally respects the laws of fluid dynamics, but NH₃ may begin to oxidize in the injected stream before mixing with the flue gas is complete.

These findings led us to the conclusion, that no single nozzle type can be found, that is fit in all cases. The final concept included the use of multiple-hole nozzles, and separate nozzle types were installed in each injection level.

MODELLING WORK

Two different approaches were made in mathematical modelling of the SNR process: a purely theoretical kinetic model based on a large number of elementary reactions, similar to Miller & Bowman [13], and an empirical approach with adjustable parameters in a simple two-reaction model [14]. The design of the quartz reactor ensured a very well-defined temperature and residence time, thus providing good experimental data for studying the reaction kinetics. This was done by comparing the experimental data with several published models.

The model of Dean et al. [15, 16] offered the best fit with experimental observations. Nevertheless, the fit was not quite satisfactory, and a new model [17] was developed. The main routes are the same as Dean et al.'s (see Figure 10), but the choice of elementary reactions has been changed, based on a sensitivity analysis, and several kinetic constants have been adjusted.

The kinetic model predicts laboratory results very well. However, for design purposes model adjustments may be desirable to allow for deviations from ideality (such as mixing effects) or use of an additive. These adjustments are not easily made on the fundamental model. A simple model was developed with just two reactions of NH₃, reflecting the two reaction routes: one in which NO is consumed and one that produces NO. Pre-exponential factors and activation energies were adjusted to the best fit with laboratory results. The model gave a satisfactory prediction of pilot-scale results. For predicting full-scale results, a global model must be used, taking into account both chemical kinetics, gas flow, and the complicated micro-mixing effects. Till now, a model has been used, predicting the mixing effects on an empirical base [2]. The results are quite good on the test boiler, but still not reliable enough to be used for design purposes.

During the last year, work has been going on to develop a theoretically based micro-mixing model. This work is still in progress and will be reported elsewhere.

The test data achieved during commissioning of the full-scale plant was used for a theoretical approach to a control strategy based on a neural network. This work, that has been reported elsewhere [18], shows a promising line for future plant control.

DISCUSSION

The present work has included a comparison between the two most important deNOₓ reductants, ammonia and urea. Several models have been proposed on the thermal decomposition of ammonia in the presence of NO, but very little
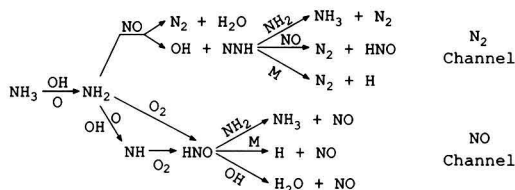
FIGURE 10. The reaction scheme of Dean et al. [15].

work has been done on thermal urea decomposition. Our experiments strongly suggest, that the decomposition of urea follows a different route than ammonia decomposition. The first decomposition step probably is [19]
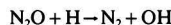
$$H_2NCONH_2 \rightarrow NH_3 + HNCO$$

followed by

$$HNCO + OH \rightarrow NCO + H_2O$$

and

$$NCO + NO \rightarrow N_2O + CO$$
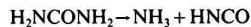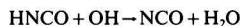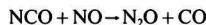
The latter reaction is known [20] to be of major importance in the formation of N₂O by combustion. However, at elevated temperatures N₂O is rapidly removed by

$$N_2O + H \rightarrow N_2 + OH$$

Thus a sharp rise in the N₂O emission shows below 950°, as the N₂O decomposition slows down. A more detailed discussion of the proposed mechanism is found in [3].

The additive experiments have shown that the SNR reactions are highly sensitive to an increase in the concentrations of C- and H-containing radicals by introduction of easily ignited additives. The additive experiments have been very extensive, but it turned out that the best choice for the final concept was the most obvious, namely natural gas. The experiments have been very important in uncovering the micro-mixing effects. It has been reported earlier [5], that some of the additive results were not reproducible in full scale. The deviations are consistent with the assumption of concentration gradients due to mixing effects in a micro-scale. Micro-mixing seems to be much more important for the process performance than supposed hitherto.

The flow in the boiler is very turbulent, causing great variations in residence time of the reductant. This condition can be successfully met by injecting natural gas somewhat downstream of ammonia injection to aid burnout of remaining ammonia. An alternative route is to abstain from the use of additives and lay greater weight on nozzle optimization. Also this concept has been proved successful, though the accessible reduction, when the slip limit has to be respected, is a little lower.

CONCLUSIONS

- The selective noncatalytic reduction method has been developed for use on coal-fired combustors.
- A regulation strategy based on boiler load as the primary feed-forward signal has been developed and successfully tested during 2000 hours of fully automatic operation.
- A NOₓ reduction level of 50 to 70% has been reached.
- NH₃ as a reductant is superior to urea, as the emissions of unwanted species are considerably lower.

- Several additives are capable of moving the temperature window of the process, but no additive was found able to broaden it.
- Natural gas may be used as a tail-end additive to reduce NH_3 slip.
- Chemical processes during the mixing period have great influence on the performance and micro-mixing must be taken into account in a practical design.

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Nitrous Oxide Sampling, Analysis, and Emission Measurements from Various Combustion Systems

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Nitrous oxide (N_2O) emissions from various combustion systems was measured by use of two analytical methods, the performance of which was evaluated together with the sampling procedures. One analytical method is grab sampling followed by analysis by gaschromatography (GC). This procedure was found to give accurate results, provided SO_2 and H_2O were removed during sampling in order to avoid N_2O formation in the sample. An evaluation of a continuous infrared N_2O analyzer shows that it is a useful instrument if measures are taken to eliminate or adjust for interferences from CH_4, SO_2, H_2O, and to a minor extent also from NH_3. A considerable formation of N_2O was found when a gas containing SO_2 and NO was scrubbed in a weak acid solution.

The sampling program from a variety of combustion systems reveals that N_2O emissions usually are low (0–5 ppm) from the combustion of pulverized coal.

The results from a gas turbine, a laboratory gas-fired fiber burner, and a domestic oil combustor are also in the very low range, whereas emissions from combustion of straw or wood were slightly higher. Even higher emissions were observed from circulating fluidized bed combustion (CFBC), from which the level of emissions increased with decreasing combustion temperature and increasing excess air levels. Sampling inside the CFBC reactor showed that N_2O formation is particularly rapid at the transition from reducing to oxidizing conditions at the secondary air inlet. Pilot plant experiments with the selective non-catalytic reduction of NO by urea or ammonia resulted in a large increase in N_2O emissions during the injection of urea, whereas almost no increase was found during the injection of ammonia.

INTRODUCTION

The emission of nitrous oxide (N_2O) from combustion has attracted attention due to its possible impact on the depletion of stratospheric ozone and on the greenhouse effect [8, 18]. Furthermore, the concentration of N_2O (currently about 305 ppb) in the atmosphere is increasing [25] at a rate of about one ppb/year.

Current N_2O emissions from stationary combustion sources contribute to 3–10% of estimated anthropogenic emissions. Other sources are the use of fertilizers, biomass burning, and mobile combustion processes, but a major part of the anthropogenic source cannot be accounts for [18].

Until 1988 the contribution from the stationary combustion sources was grossly overestimated due to an erratic sampling procedure, which was grab sampling with no treatment of the

gas. When using grab sampling for N_2O analysis there is a risk of N_2O formation in the sample during storage, the so-called 'sampling artifact' [5, 9]. The sampling artifact resulted in a much too high estimate of emissions particularly from the combustion of fuels containing sulfur, since it occurs due to the simultaneous presence of NO, SO_2, and H_2O in the sample. It was shown by de Soete [5] that the artifact is avoidable by on-line analysis or by quantitative removal of SO_2 and H_2O.

In on-line continuous monitoring by infrared analysis, the artifact is avoided, but the method involves the risk of interference from other components present in the gas. For this reason, the performance of a commercially available IR analyzer is evaluated in the laboratory as a part of this paper.

By removing SO_2 and H_2O from the sample, the correct emission values from pulverized coal, oil or liquid natural gas firing were found to be 0–5 ppm [9, 18, 28]. No records of emissions from combustion of straw in larger combustion units or from a natural gas fired fiber burner have been found in the literature.

Certain deNO$_x$ technologies produce N_2O. For instance, Zel-

linger and Tauschitz [29] found considerable N$_2$O production during the injection of urea for the selective non-catalytic reduction of NO (SNR) in a large-scale pulverized coal unit. During the injection of NH$_3$ in the same type of process, only small amounts of N$_2$O were measured by Sun [26] and Muzio [23] in small-scale units. No data are reported for the formation of N$_2$O when injecting additives together with ammonia.

The scope of this study is to validate procedures for the sampling and analysis of N$_2$O, to increase the database on N$_2$O emissions from various combustion systems and to gain knowledge of N$_2$O emissions from the SNR process and circulating fluidized bed combustion (CFBC). For sampling and analysis, both the off-line method followed by GC analysis and the on-line IR analysis were used for N$_2$O emission measurements from a range of combustion systems.

SAMPLING PROCEDURES

Different kinds of sampling probes were used, depending on the sampling environment. For emission measurements at low temperatures it was simply a teflon tube.

When sampling from a hot environment, such as the bed of a fluidized bed combustor, decomposition of N$_2$O over the hot filter may be a significant problem. For this reason, a probe with a cooled filter for gas (and particle) sampling in FBCs was designed. This probe has been tested extensively by Bank and Dam-Johansen [2], where the conversion of CO and NO over the filter of the probe was found to be very small compared to that of a probe with a non-cooled filter. Bank and Dam-Johansen did not include N$_2$O in their work. During sampling in the bed of a CFBC (reported below), the performance of the two types of probes were compared further. The probes were placed in pairs at different heights. The N$_2$O concentration measured using probes with cooled filters was higher than when using the non-cooled probes, indicating N$_2$O decomposition over the non-cooled filter.

Certain treatments of the gas are necessary during sampling to avoid N$_2$O formation. In grab sampling, a scrubbing flask with 1 M Na$_2$CO$_3$ was used to absorb SO$_2$. Ice was added to the flask in order to condense some of the water vapor. Mg(ClO$_4$)$_2$ removed most of what was left. The sample was then collected in a 10 liter Tedlar (polyvinyl fluoride) bag and analyzed using gas chromatography (GC). No artifact N$_2$O formation was observed in these samples over the course of a week.

In on-line IR analysis removal of SO$_2$ (and NH$_3$) and control of the H$_2$O content of the gas are desirable for reliable N$_2$O analysis as discussed in the next section.

ANALYSIS

Gas Chromatography

The gas chromatograph was equipped with a 3.7 m Porapak Q packed 0.32 cm stainless steel column maintained at 50°C. Injection into a 14 mL/min He flow took place via a gas sampling valve with a 1 cm^3 sample loop maintained at 125°C. A thermal conductivity detector (TCD) maintained at 125°C was used for detection.

In order to simulate combustion flue gas analysis, the GC was calibrated with an N$_2$O/N$_2$ mixed gas diluted with N$_2$ and CO$_2$ to yield 15% CO$_2$ and 0–500 ppm N$_2$O. CO$_2$ was added because it is the strongest interfering component. A deviation of up to 3% was found with no CO$_2$ present, showing only a slight influence. The detection limit was 2 ppm. The deviations from linearity were usually within ±1 ppm in the range 0–100 ppm. The uncertainty of the N$_2$O concentration calculated from flow measurements could account for most of this deviation. Occasionally single analysis points were in large error. Therefore, at least double analysis was performed for accurate results.

Not including the tolerance of the calibration gas, the estimated accuracy of the GC measurement is ±2 ppm for the range 0–100 ppm. Above 100 ppm, there is an estimated ±2% accuracy.

The gas chromatography method adopted in this study gives sufficiently accurate measurements even at low concentrations, particularly due to the lack of strongly interfering components in combustion gases. The analysis, however, is time consuming and non-continuous and there is a risk of N$_2$O formation within the sample containers prior to analysis.

Infrared Analysis for N$_2$O

The continuous infrared analyzer (Perkin-Elmer Spectran 647) is a one-beam, NDIR-type, bifrequency analyzer with an optical path of six meters [3]. The measuring and reference wavelengths are 7.8 and 8.22 μm, respectively. Interference is possible at both of these wavelengths.

The instrument is calibrated with N$_2$O/N$_2$/H$_2$O mixture containing the water that remains after condensation at 2°C. In the 0–100 ppm linearity test, all points are within a ±1 ppm deviation from a straight line. This is within gas mixing accuracy. In the high range, 0–500 ppm, the linearity is not quite as good, with up to about a 2% deviation from a straight line.

Interfering Gases

The IR instrument was evaluated for interferences by investigating the potentially interfering gases one by one at various concentrations. In most cases, the evaluation was performed at a constant concentration of N$_2$O, and with water condensed at 2°C. In Figures 1 and 2, the results are plotted as the error in ppm N$_2$O. Each point represents the error calculated as "instrument signal" minus "the true N$_2$O concentration calculated from flow measurements."

Figure 1 represents the most significant case, showing a strong interference by SO$_2$. This could be either a positive or a negative interference, depending on the concentrations of both SO$_2$ and N$_2$O. Judging by the infrared spectra, the interference was expected to be negative, since the reference wavelength is on the edge of an SO$_2$ peak. However, the in-
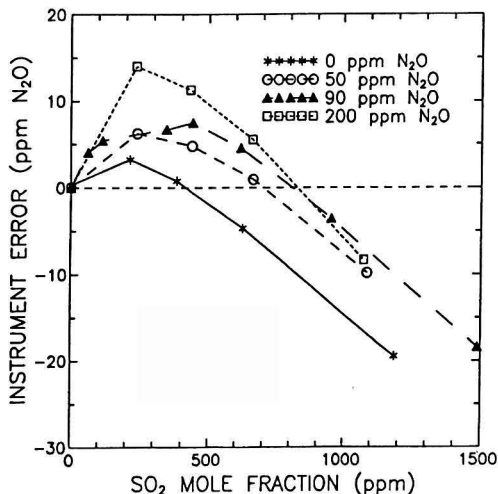

FIGURE 1. Interference from SO$_2$ in IR analysis. Deviations from the true concentrations. 0 to 1500 ppm SO$_2$ at 0, 50, 90, and 200 ppm N$_2$O and water condensed at 2°C.
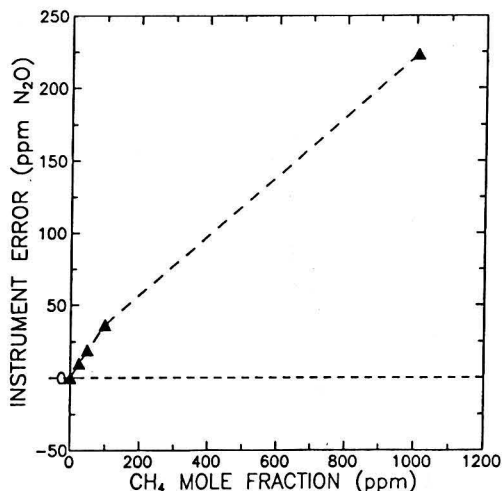
FIGURE 2. Interference from CH_4 in IR analysis. Instrument signal for 0 to 1000 ppm CH_4 at 0 ppm N_2O and water condensed at 2°C. Zero is for N_2 and water condensed at 2°C.
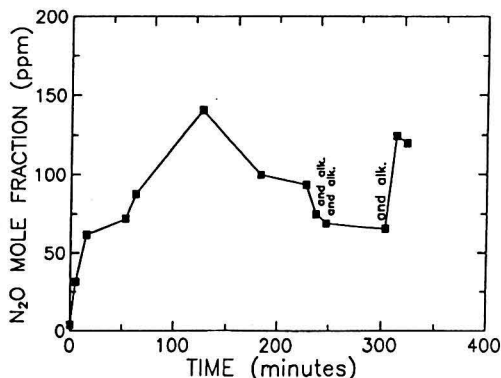

FIGURE 3. N_2O formation when a gas containing high concentrations of NO and SO_2 is bubbled through a flask containing a weak acid solution. Solution: 0.058 M H_2SO_4. Artificial gas mixture. Gas concentrations: 1465 ppm NO, 1368 ppm SO_2, 7.8% O_2, 11.9% CO_2, 4 ppm N_2O. Flow: 282 mL/min at 1013 mb and 298 K. N_2O analysis by on-line GC-TCD. Points "and alk.": acid scrubbing was followed by a 1 M Na_2CO_3 scrubber.

terference turned out to be positive for low SO_2 concentrations. SO_2 can be removed by scrubbing the gas in a 1 M Na_2CO_3 solution, which should be placed upstream from the water condensation device, because water is another highly interfering component. The water content is therefore kept constant by condensation at a fixed temperature.

NH_3 is another interfering component which is fairly straightforward to control. Although not studied in detail, 600 ppm NH_3 resulted in a negative signal of about 10–12 ppm on the N_2O analyzer, both at 0 ppm and at 200 ppm N_2O. If water condensation takes place, most of the NH_3 is dissolved in the condensate. When an acid scrubber is used for NH_3 removal, it is placed after the alkaline scrubber due to the risk of a scrubbing solution artifact, as discussed in the next section.

If a large amount of methane (CH_4) is present, interference can be a severe problem as shown in Figure 2. Unlike H_2O, SO_2, and NH_3 it is difficult to remove CH_4 by chemical means without influencing N_2O. In combustion flue gas this is rarely a problem, but when making in-bed measurements in a fluidized bed combustor, large amounts of CH_4 could render the N_2O analysis useless. When the SNR process with natural gas as an additive was studied, the interference from CH_4 was given special attention.

The interference from each of the gases NO, CO, CO_2 and O_2 was found to be positive and less than 2 ppm (probably even less than 1 ppm) at any concentration relevant to combustion [13]. Similarly, no detectable interference was found from 1265 ppm HCN in N_2.

Although most of the interference can be controlled, IR analysis is not useful in detecting absolute levels where N_2O emissions are low, as in pulverized coal combustion. On the other hand, it is useful for the detection of changes following various NO_x control strategies, for example. It is also useful as emissions monitor during fluidized bed combustion, where emissions usually are somewhat higher, causing the relative error from interference to be of minor importance.

SCRUBBING SOLUTION N_2O FORMATION

As reported in the previous section, the elimination of interference during on-line IR analysis also includes the removal of NH_3 when present, e.g., by scrubbing in a weak sulfuric acid solution. However, if SO_2 is not removed before the scrubber, an N_2O formation could occur in this solution.

In Figure 3, an artificial flue gas containing NO, SO_2, O_2, and CO_2 was bubbled through a 250 mL flask at about 20°C containing a weak acid solution of 0.058 M H_2SO_4. The scrubbing was followed by condensation of H_2O at 0°C in an ice bath. A part of the gas stream was then directed through the sampling loop of the GC for immediate analysis. The total residence time of the gas in the system was less than one minute. As shown in Figure 3, the use of a gas containing high concentrations of NO and SO_2 caused a pronounced N_2O formation. About 60 ppm was formed after only 20 minutes, and after further bubbling more than 100 ppm was formed, corresponding to almost 20% of the content of N in the NO.

It is remarkable that when the acid scrubbing is followed by alkaline scrubbing (points marked "and alk."), in which SO_2 is removed, the N_2O level is lower than without alkaline scrubbing. This indicates that without the SO_2 scrubber some of the N_2O formation occurs in the line after the acid scrubber, i.e., in the water condensation line, in the line to the GC, in the sample loop, or even in the first part of the GC-column after sample injection. The formation of N_2O was barely detectable over two hours of bubbling, when the gas contained lower concentrations of NO and SO_2, 346 and 322 ppm, respectively, and the gas flow rate was increased to 750 mL/min.

If a flask containing an alkaline scrubbing solution was placed before the acid scrubber, no detectable formation of N_2O was seen over more than 10 hours at conditions similar to the ones shown in Figure 3. The N_2O level during acid scrubbing of a gas containing 1500 ppm NO but no SO_2 did not increase over more than 160 minutes, indicating that SO_2 is a key component in the formation of N_2O. The fact that the N_2O formation depends on the amount of SO_2 present is in agreement with studies of N_2O formation in grab samples [5, 24].

The scrubbing solution artifact could not only cause problems during analysis. These results give rise a suspected possible N_2O formation from industrial acid scrubbers, of which no N_2O emission study has been found by the authors in the literature.

RESULTS OF THE N_2O MEASUREMENTS

Table 1 lists the main results of the emissions measurements. A more detailed tabulation of the results from each plant is

Table 1 Results of N₂O emissions measured by gas chromatography of bag samples. Values are for a dry gas corrected to 6% O₂

Site	Emissions vol. ppm N_2O, dry
Pulverized coal:	
DTH heat and power station, 5 MWe	2–5
NEFO-I, 135 MWe	3
Fynsværket II, 205 MWe	≤2
Studstrup-III, 350 MWe	
before spray absorption FGD	≤2
after spray absorption FGD	≤2
Amager-III, 215 MWe	
before wet limestone FGD	≤2
after wet limestone FGD	≤2
Natural gas:	
Frederikshavn, turbine, 17 MWe	≤7[*]
Fiber burner, laboratory scale	≤2
Straw:	
Haslev, 5 MWe	6 ± 5
Other combustion systems:	
Risø, circulating fluidized bed, 2 MWt	25–150
NEFO-1, pilot plant with injection of NH_3[**]	10
NEFO-1, pilot plant with injection of urea[**]	70
Dry SO_2 removal by NH_3 at 40–70°C	≤2
Domestic gas oil fired	≤2.5[*]
Domestic furnace, beech wood, flaming	13 ± 5
Same, smoldering	≤15[*]
Spruce burning for central heating, domestic	≤6[*]

[*]: bag sample analysis showed ≤2 ppm. Larger uncertainty is introduced when correcting to 6% O_2, due to large amounts of excess air.
[**]: at the temperature for maximum NO reduction.

found in Hulgaard [14]. Little if any N₂O is seen from the five plants burning bituminous pulverized coal. This result fits in well with the resulted published [18, 28]. The application of low-NOₓ burners in Amager-III does not seem to increase N₂O emissions.

That no emissions were found from natural gas firing in a turbine was also in agreement with what we found in the literature. No N₂O emission was observed from a laboratory scale natural gas fired fiber burner at a load of 79–243 kW/m² and stoichiometric ratios of 1.05 to 1.16. Slight N₂O emissions were measured from straw combustion, in which bales of straw are burned from one end to the other while being pushed slowly into the combustor. The emissions from two small domestic wood stoves were also studied. Little N₂O was found to be emitted from the combustion of spruce in a combined wood and oil combustor used for central heating. In another stove burning beech wood, a slight N₂O emissions was found during flaming, while the emissions during the smoldering phase were not detectable, i.e., the analysis showed a not detectable level in the samples, but due to a high oxygen concentration in these samples, the correction to 6% O₂ amplified the uncertainty.

The data are in agreement with other data on biomass burning, including FBC, with 0–20 ppm from wood burning [1], and including simulated open air combustion of a variety of biofuels with 1–17 ppm at 12% CO₂ (derived from the data of [19]).

Flue gas desulfurization in pulverized coal fired units did not seem to affect N₂O emissions, neither from a wet limestone/gypsum process, nor from the Ca(OH)₂ spray absorption process, nor from a process in which SO₂ is removed by ammonia at a low temperature (40–70°C) and under dry conditions. The product in the last process is primarily ammonium

sulfate. Further details on this process were presented by Hjuler [10] and Hjuler and Dam-Johansen [11].

Significant emissions were seen, however, from fluidized bed combustion and from the injection of urea in the selective non-catalytic reduction of NO, which will be dealt with in the following sections.

Risø Circulating Fluidized Bed Combustor

The Risø unit (Figure 4) is a 2 MWt coal and straw fired CFBC based on the concept of a multi-circulating fluidized bed combustor described by Holm and Clausen [12]. The concept was developed by Aalborg Ciserv International A/S and it includes a pre-separation of particles between the riser and the cyclone. The pre-separated particles are collected in a bubbling fluidized bed, from which they are returned to the riser through an L-valve. The bubbling bed also acts as a particle cooler. The coal used was a low sulfur bituminous coal with 35.9% volatile matter (dry ash free), please see Table 2.

"Fakse Bryozo" limestone, 80% (by weight) of which had a particle size of 2–80 μm, was used for desulfurization. This limestone is 97% (by weight) CaCO₃ and 1.5% MgCO₃, it is described in more detail and its reactivity towards SO₂ capture compared with other limestones in Dam-Johansen and Øster-gaard [4].

Table 2 Coal analysis, based on the coal as delivered

	% by weight
Water, total	10.4
Ash	9.8
Sulphur	0.53
Hydrogen	3.7
Carbon	65.7
Nitrogen	1.6
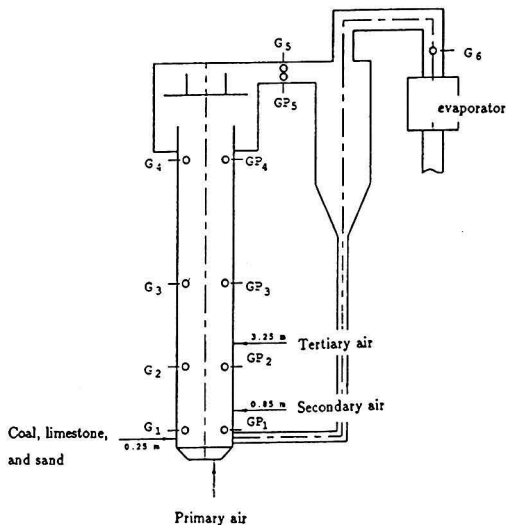
FIGURE 4. Schematic of the 2 MW CFBC and of the positioning of probes for gas and particle sampling. G: uncooled probes for gas sampling, GP: water cooled probes for simultaneous gas and particle sampling. GP_1, $G_1 \cong 0.4$ m; GP_2, $G_2 \cong 2.8$ m; GP_3, $G_3 \cong 5.0$ m; GP_4, $G_4 \cong 9.2$ m; GP_5, G_5 before the cyclone; C_6—after the cyclone.
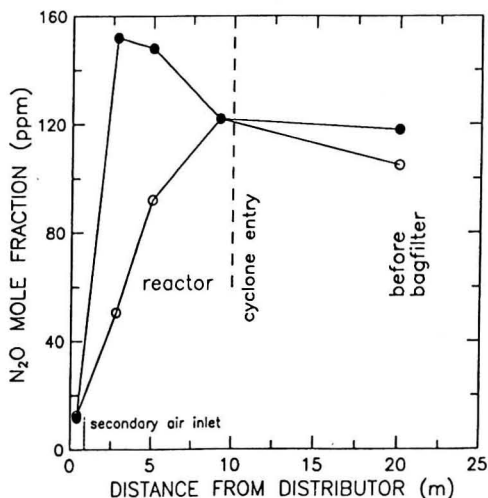
FIGURE 5. Measurement of N_2O in the Risφ 2 MWt CFBC by off-line GC analysis. GC results are the measured values (o) or values transformed to 15% CO_2 (•). Addition of limestone: Ca/S = 2.5; bottom bed temperature: 845°C, reactor top temperature: ca 870°C. Emissions: 4.0% O_2, 205 ppm CO, 15.2% CO_2, 154 ppm NO. 36% primary air, 64% secondary air, no tertiary air.

Air was introduced as primary, secondary, and tertiary air. The probes used for gas sampling in the reactor had a cooled filter, as described previously. A few examples of concentration measurements will be given in order to illustrate common trends.

The N_2O Profile Through the Reactor

Figure 5 shows the results of sampling and analysis at different heights in the fluidized bed. The samples were analyzed both on-line by IR and off-line by GC. Heights above 10 meters are outside the riser part of the reactor, 20 meters is for emissions. The IR results have been omitted from Figure 5. After correction for the contents of CH_4 and SO_2, the IR results are within ±20 ppm of the GC results for the in-bed measurements. The accuracy is not as good as for flue gas analysis, especially due to the large correction necessary for CH_4, as discussed above. The values obtained by GC analysis are considered to be quite accurate and are used as the "true" N_2O content. Figure 5 shows that little N_2O is formed in the dense bed, where reducing conditions exist. A great deal of N_2O is formed after the secondary air inlet, at 0.85 m.

When data are used as measured, there is a gradual increase in N_2O concentration throughout the riser. This corresponds closely to the profiles presented by both Åmand et al. [30] and Moritomi et al. [22]. However, a different pattern emerges when correcting to 4% O_2 (corresponds closely to 15% CO_2 as used in Figure 5) throughout the reactor. The difference between the curve for the measured values and for the one obtained after correction to 4% O_2 is particularly pronounced at the 2.8 m and 5.0 m sampling levels, where high O_2 concentrations were measured. There are two potential reasons for the high O_2 level.

First, it could represent the true gas phase concentrations at the sampling levels. The correction to 4% O_2 then corresponds to considering that any oxygen in excess of 4% represents merely dilution, which in turn ascribes the N_2O formation to the total consumption of O_2 at the sampling spot. This can be explained by the fact that the correction to 4% O_2 is performed by multiplication of the measured concentra-

tion by $(0.21 - 0.04)/(0.21 - X_{O_2})$, where X_{O_2} is the mole fraction of O_2 measured. From Figure 5 it appears that the N_2O formation relative to the O_2 consumption is larger in the first part of the reactor (after the secondary air inlet) than in the last part. Let us suppose that the oxygen consumption occurring from 0.4 to 2.8 m is primarily caused by oxidation of volatile species. Even if this is only partially true, and even if N_2O decomposition takes place throughout the reactor, combustion of the volatiles contributes significantly to the N_2O formation in this FBC.

A significant influence of the volatiles was also found by Wójtowicz et al. [27]. In their laboratory FBC burning a range of coals and chars, more N_2O was formed from the combustion of coal than from the chars derived from the same coals.

Another explanation of the high O_2 concentration at 2.8 m and 5 m could be stratification, in which there are large radial concentration gradients in the reactor. The probe tip was 15 cm from the center (20 cm from the wall). No radial profiles were measured, but other researchers found large radial gradients, e.g., Åmand et al. [30]. However, even if gradients exist, the concentration still represents the gas at the point sampled from.

Dependence on Bed Temperature

In Figure 6 emissions of N_2O are plotted as a function of bed temperature. N_2O emissions decrease with increasing temperatures in agreement with data from the literature [21, 31].

Dependence on Excess Air Level

In Figure 7 the N_2O emission can be seen to increase with the oxygen level. Unfortunately other parameters also changed with the changing O_2 content, although the stoichiometry in the lower part of the reactor was kept constant: for instance, the linear gas velocity and the temperature at the top of the reactor changed. These relatively small changes are, nevertheless, unlikely to be responsible for the entire relationship. In-
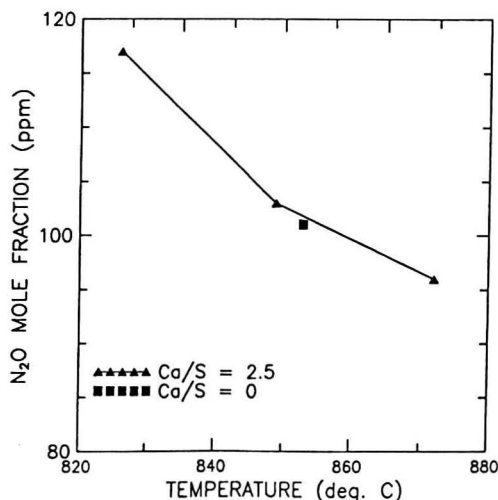
FIGURE 6. The temperature dependence of N_2O emissions in the Risφ CFBC. O_2: 4.0%; equivalence ratio after the secondary air inlet: 0.8. The remaining oxygen is introduced as tertiary air. The temperature is the bottom bed temperature. N_2O values are obtained by on-line IR analysis and adjusted for interference from SO_2 and CH_4
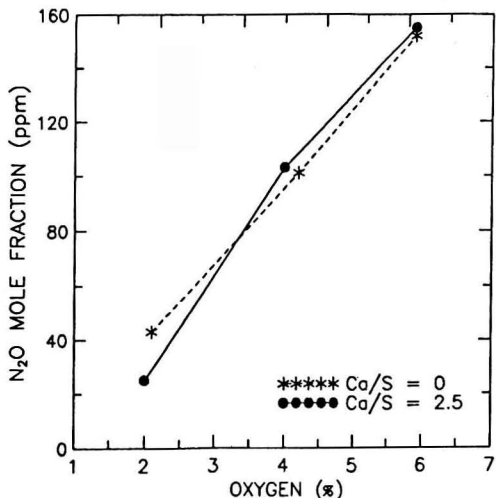
FIGURE 7. N$_2$O emissions versus oxygen in the outlet of the Risφ CFBC reactor. Equivalence ratio after the secondary air inlet: 0.8. The remaining oxygen is introduced as tertiary air. N$_2$O values obtained by on-line IR analysis and adjusted for interference from SO$_2$ and CH$_4$ and transformed to 4.0% O$_2$. Bottom bed temperature: 850°C.

creasing N$_2$O emissions with increasing excess oxygen levels are in agreement with the results of Åmand and Lecker [31] from a 12 MWt CFBC. They extracted the data points at times when the reactor top and bottom temperatures were kept within narrow limits.

These results indicate that N$_2$O emissions could be reduced by lowering the excess air ratio, which also reduces NO emissions. However, very low excess air levels may cause CO emissions to increase and detriment the SO$_2$ retention.

Results of the Selective Non-Catalytic Reduction of NO

In a large number of experiments, ammonia or urea were injected at high temperatures in order to selectively reduce NO by a non-catalytic process, the SNR process described previously [20, 6, 7].

The experiments were performed in a pilot plant in which about 600 kg/h of flue gas was extracted at 1100°C from a 135 MWe pulverized coal fired boiler [16, 17]. The gas was cooled at a rate of 200 K/s as in the full-scale boiler. The reductant injection point was adjusted in order to obtain different injection temperatures.

Ammonia Injection

Figure 8 shows results from the injection ammonia at a molar ratio of NH$_3$/NO equal to 1.3. N$_2$O emissions were between 10 and 15 ppm. The base level without ammonia injection was 5–10 ppm, measured by on-line IR. In other words, a slight increase was observed over the entire 800–1000°C temperature range. This increase does not seem to depend on the extent of NO$_x$ reduction. At the optimum level of NO reduction the relative N$_2$O production (2·ΔN$_2$O/ΔNO) is about 5%.

There is no pronounced N$_2$O peak in this study. In the studies of both Muzio [23] and Sun [26], a peak occurred at around 870°C (1145 K), and a relative N$_2$O production of about 10% was found at the peak for NO reduction. A higher NH$_3$/NO molar injection ratio in these studies (around 2, compared to 1.3) could explain the higher relative N$_2$O production.
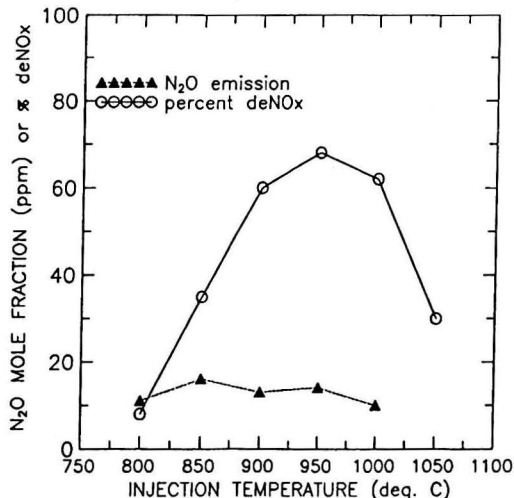
FIGURE 8. NO$_x$ reduction and emissions of N$_2$O at a NH$_3$/NO molar ratio of 1.3 in the SNR pilot plant. Reductant: ammonia. The NO$_x$ base level is about 320 ppm. O$_2$ = 6%, SO$_2$ = 650 ppm.

The pilot plant results shown in Figure 8 correspond closely to the following full scale results, in which also about 10 ppm N$_2$O was found at an NH$_3$/NO molar ratio of 1.3.

The results also match those from a flow reactor laboratory study of the reactions between NH$_3$ and NO in mixtures of pure gases [15]. At an NH$_3$/NO molar ratio of 1.35 an N$_2$O formation of about 10 ppm was found at the temperature of maximum NO reduction. Also in this case, this corresponds to a relative N$_2$O production of about 5%.

Urea Injection

When urea is used as reductant instead of ammonia, much higher N$_2$O emissions are observed (Figure 9). N$_2$O emissions follow the reduction of NO$_x$ to some extent, although the peak
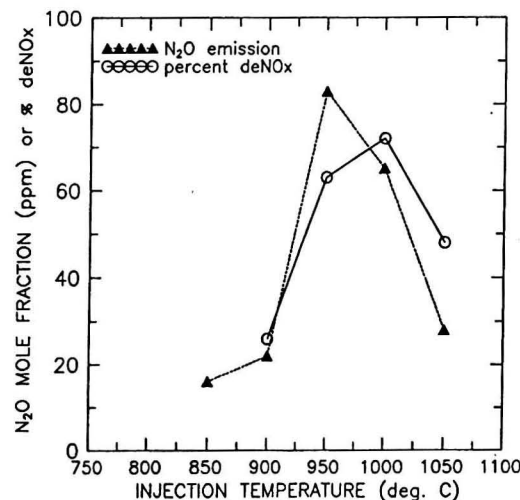
FIGURE 9. NO$_x$ reduction and emissions of N$_2$O at a NH$_3$/NO molar ratio of 1.3 (N in urea/NO) in the SNR pilot plant. Reductant: urea. The NO$_x$ base level is about 400 ppm, O$_2$ = 6%, SO$_2$ = 650 ppm.
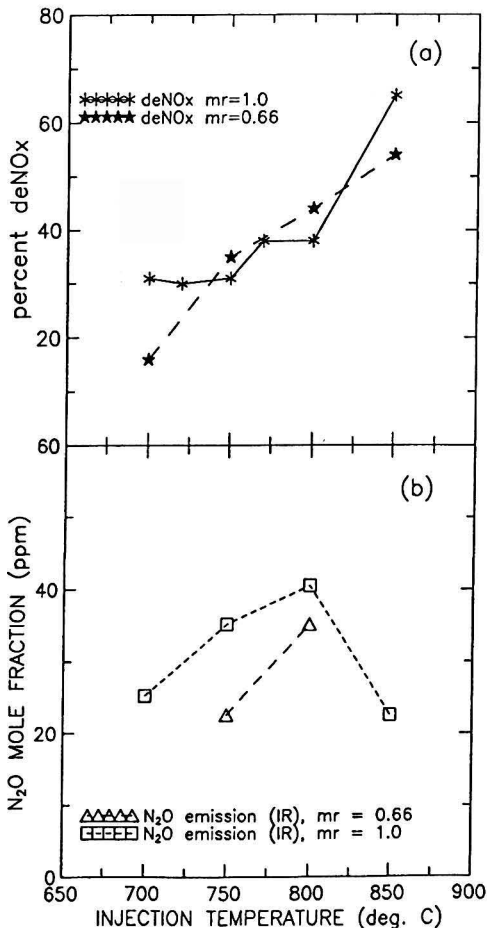
FIGURE 10. Percent deNO$_x$ (a) and emissions of N$_2$O (b) during injection of ammonia and ethanol in NH$_3$/NO and ethanol/NO molar ratios of 1.6 and mr = 1.0 or 0.66, respectively. The base level of NO$_x$ is about 450 ppm. Analysis for N$_2$O was by on-line IR analysis with SO$_2$ removed in an alkaline scrubber but no adjustment for methane. O$_2$ = 6%, SO$_2$ = 650 ppm.

at 85 ppm N$_2$O is at a lower temperature than the peak for NO$_x$ reduction. The peak value corresponds to conversion into N$_2$O of more than half of the reduced NO$_x$. The results indicate that the relative N$_2$O production could be reduced by injecting at a higher temperature than would otherwise be used. This would, however, narrow the temperature window even further.

In agreement with these results, Zellinger and Tauschitz [29] found about 50% relative N$_2$O production in a utility boiler by use of a urea solution as reductant at a molar ratio "N in urea"/NO of about 2.

Injection of Additives Together with Ammonia

In the following experiments, additives were injected together with ammonia in order to obtain the reduction of NO$_x$ at lower temperatures than indicated in Figure 8. The effect of natural gas, methane, butane, ethanol, and other gases was investigated. Figure 10 is a representative example of the deNOx-percent and N$_2$O emissions using ethanol and ammonia. The peak deNOx percent was not found in this experiment,

but it was found to be at 850–950°C from tests made on another day.

N$_2$O emissions were usually higher than with ammonia injection alone, but not as high as with urea injection. The relative N$_2$O production was about 10–40%, lowest at the higher temperatures.

N$_2$O emissions higher than those found with pure ammonia were also found for the other additives tested, but the increase was usually smaller than with the additive ethanol.

Natural gas injection together with ammonia in a full scale (135 Mwe) boiler caused only a minor (<5 ppm) increase in N$_2$O emissions compared to ammonia injection alone.

CONCLUSION

The sample program upon which this paper is based confirmed that N$_2$O emissions are low from pulverized coal combustion, a natural gas fired turbine, a natural gas fired fiber burner, and straw combustion.

Flue gas desulfurization by a wet CaCO$_3$/gypsum process, by Ca(OH)$_2$ spray absorption, or by dry ammonia injection at a low temperature did not cause detectable N$_2$O production.

A small increase in N$_2$O was observed in the SNR process using ammonia as reductant. Additives together with ammonia were found to cause a further slight increase in N$_2$O emissions, and still higher emissions were observed with urea as a reductant. N$_2$O emissions may be reduced by injection of the reductant at higher temperatures than otherwise used.

A relatively high level of N$_2$O emissions was seen from fluidized bed combustion. N$_2$O emissions increased with decreasing temperatures and with increasing stoichiometry. Even at constant bed temperatures and oxygen levels, results from the combustor studied varied greatly, indicating that other factors may influence N$_2$O emissions.

Analysis of N$_2$O from combustion systems was performed by on-line analysis or grab sampling followed by GC analysis. Grab sampling required special care, since SO$_2$ and H$_2$O had to be removed prior to collection in a sample container in order to avoid N$_2$O formation in the container during storage.

In the setup used, a GC detection limit of about 2 ppm was found, and little interference was seen—only from CO$_2$. GC analysis is, however, non-continuous and time consuming.

The continuous IR analyzer operating at 7.8 μm is faster, but suffers from interference particularly from CH$_4$, SO$_2$, H$_2$O, and NH$_3$. Only CH$_4$ cannot be dealt with by scrubbing or condensation. The instrument is therefore particularly useful as an emissions monitor where N$_2$O emissions are high and CH$_4$ is absent or measured simultaneously, and in controlled conditions in laboratories.

For use in future emissions studies and in sampling systems, attention should be paid to the possibility of N$_2$O formation during acid scrubbing of a gas containing SO$_2$ and NO.

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Anaerobic/Aerobic Biological Activated Carbon (BAC) Treatment of a High Strength Phenolic Wastewater

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As a result of manufacturing operations at the Durez Division of Occidental Chemical Corporation (OCC) located in North Tonawanda, New York, a highly phenolic wastestream is produced. At the time of this study, average phenols and total COD concentrations of the wastestream averaged 35,000 and 10,000 mg/L. Studies were conducted at the Durez Facility to assess sequenced anaerobic/ aerobic biological activated carbon (BAC) process treatment of this wastestream. The first stage anaerobic BAC process achieved significant organic conversion with minimal solids production, and near stoichiometric methane production. Excellent polishing of the AnBAC process effluent was achieved in the aerobic BAC unit even under variable influent conditions. Effluent filterable COD from the aerobic BAC process averaged 165 mg/L and was speculated to be primarily non-biodegradable soluble metabolic endproducts. Effluent phenols from the process typically were below 0.01 mg/L and averaged 0.04 mg/L. Overall process efficiency for total COD, filterable COD, and phenols were >97, >99, and approximately 100 percent, respectively.

INTRODUCTION

The Durez Division of Occidental Chemical Corporation (OCC) located in North Tonawanda, New York manufacturers phenolic resins and phenol molding compounds. A thermoplastic and thermoset type resin, used in the manufacture of automobile and appliance parts requiring high temperature performance, is the principal product from the plant. The primary raw materials are phenol and formaldehyde, and these two compounds carry over into a strong liquor produced from process off-gas scrubbing. Currently the strong liquor is stripped of phenol and incinerated onsite or transported out of state for biological treatment.

Due to the difficulties associated with interstate transport of industrial wastes and the high cost of incineration, Occidental Chemical Corporation wished to explore the feasibility of alternative treatment options. Because the feasibility of

untreated strong liquor discharge into the North Tonawanda, New York POTW was uncertain, testing of an on-site treatment process was needed. To conserve space and energy, a sequenced anaerobic/aerobic biological activated carbon (BAC) process was conceptualized and proposed for study. The purpose of this paper is to report the results from pilot scale studies conducted at the Durez facility to assess the sequenced anaerobic/ aerobic treatment of strong liquor.

BACKGROUND

Waste Characterization and Flows

Strong liquor is produced at the OCC Durez facility as a result of scrubbing operations on off-gas produced during hot flaking of phenolic resins as shown in Figure 1. Long term

FIGURE 1. Schematic of strong liquor production at OCC Durez and typical waste quantity and composition.
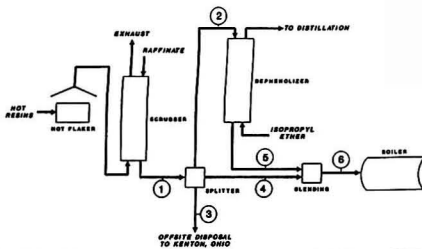
Stream No.	Designation	Annual flow, gallons	Typical concentration, mg/L			
			Phenol	Formaldehyde	Methanol	Isopropyl ether
1	Strong liquor	720,000	15,000	2,000	2,500	0
2	Strong liquor	180,000	15,000	2,000	2,500	0
3	Strong liquor	360,000	15,000	2,000	2,500	0
4	Strong liquor	180,000	15,000	2,000	2,500	0
5	Raffinate	180,000	3,000	2,000	2,500	1,000
6	Blended raffinate	360,000	9,000	2,000	2,500	500

average concentrations of phenol, formaldehyde, and methanol in the strong liquor are 15,000 mg/L, 2,000 mg/L and 2,500 mg/L, although there is considerable fluctuation in these values from batch to batch. After scrubbing, the strong liquor is sent to a blending tank where it is mixed with other waste streams. A strong liquor waste stream of between 2 to 3 gallons per minute is generated during production of the phenolic resins. Approximately 720,000 gallons of strong liquor are produced yearly.

At the present time, approximately one-half of the strong liquor is treated at the Durez facility. The remaining 360,000 gallons/year is transported, by rail cars and truck, to Kenton, Ohio where it is mixed with other phenolic wastewaters. The combined waste is then subjected to aerobic biological treatment in an activated sludge system equipped with surface aerators.

Of the 360,000 gallons of strong liquor treated at the Durez facility yearly, approximately one-half undergoes phenol extraction in the dephenolizer as shown in Figure 1. Phenol removal is achieved by counter-current extraction with isopropyl ether. Isopropyl ether containing the extracted phenol is collected at the top of the dephenolizer and sent to a distillation unit.

After dephenolization the composition of the strong liquor is changed and contains approximately 3,000 mg/L phenol, 2,000 mg/L formaldehyde, 2,500 mg/L methanol, and 1,000 mg/L isopropyl ether. This waste stream is referred to as raffinate. Raffinate is used as the scrubber fluid during production of strong liquor.

The raffinate, and strong liquor not subjected to dephenolization, are recombined and sent to a boiler for incineration. The operating temperature of the boiler is 750°C. The blend of the strong liquor and raffinate produces a yearly waste stream of 360,000 gallons/year having an average composition of 9,000 mg/L phenol, 2,000 mg/L formaldehyde, 2,500 mg/L methanol, and 500 mg/L isopropyl ether.

Previous Experience with Sequenced Anaerobic/Aerobic Treatment

Historically, anaerobic treatment of high strength industrial wastes has been of interest because of advantages associated with low sludge yield, methane production, and elimination of oxygen supply requirements. Unfortunately, anaerobic processes typically are not capable of producing an effluent suitable for direct discharge. Accordingly, to capitalize on the inherent advantages associated with anaerobic treatment while maintaining high effluent quality, studies have been conducted

to assess the feasibility of sequenced anaerobic/aerobic treatment. A number of these studies are highlighted in this section.

Several studies have explored the use of sequential anaerobic/aerobic treatment of papermill or related wastes. In a study conducted by Vuoriranta et al. [1], a first stage up-flow anaerobic sludge blanket (UASB) reactor was found capable of reducing the influent soluble COD, which ranged from 3,800 to 4,800 mg/L, by 60 to 70%. The COD remaining after anaerobic treatment was reported to be approximately 50% volatile acids. An additional 40 to 55% COD reduction was achieved in the subsequent aerobic activated sludge reactor which provided good treatment despite variations in UASB reactor performance. Huster and Mobius [2] computed costs for a sequential anaerobic/aerobic treatment of papermill wastewater and found this option to be more cost effective than aerobic treatment alone even when biogas production and sludge disposal costs were neglected. Haberl et al. [3] compared the use of sequenced anaerobic/aerobic treatment for a fiberboard industrial waste. First stage anaerobic processes were capable of achieving 65 to 70% COD removal. The subsequent aerobic activated sludge process achieved 68 to 85% COD removal. In contrast a parallel two stage aerobic process achieved COD removal efficiencies between 60 and 88%.

Bode [4] found that the effluent qualities achieved for pectin, sugar, and animal pulp industrial wastewaters subjected to solely aerobic treatment were better than those from sequential anaerobic/aerobic treatment. Heijnen et al. [5] studied a full scale three stage sequenced anaerobic/aerobic process for the treatment of an industrial waste containing COD, kjeldahl nitrogen, and sulfate. All three units employed immobilized biomass to reduce process size. The first two units were for anaerobic pretreatment and were followed by an aerobic unit primarily for ammonium and sulfide oxidation. Approximately 86% COD removal was achieved in the two anaerobic reactors. In the aerobic reactor, 100% fatty acid and sulfide oxidation, and 96 to 98% nitrification were achieved. COD removal percentage values for the subsequent aerobic reactor were not reported. le Hy et al. [6] reported good removal of nitrogen in a combined anaerobic/aerobic process applied toward the treatment of a piggery and cheese dairy wastewater. The majority of nitrogen removal was achieved in the second stage aerobic unit. COD removal for the anaerobic, aerobic, and combined process averaged 66, 91.3, and 98%, respectively.

Inamori et al. [7] reported better than 75% nitrogen removal from domestic sewage subjected to sequenced anaerobic/aerobic treatment. Approximately 70% BOD removal (200 mg/L influent) was achieved under an organic loading of 0.2 kg BOD/m³-d and a hydraulic detention time of 30 hours. Okubo et al. [8] studied the influence of daily variation of flow and pollution load on the performance of a submerged anaerobic/aerobic biofilm system. The dissolved organic carbon (DOC) in the anaerobic effluent was found to fluctuate with daily variation in flows and organic load, however, the aerobic filter linked to the anaerobic filter achieved a consistently good DOC effluent despite these variations.

Dienemann et al. [9] employed a sequenced anaerobic/aerobic fixed-film system to treat a hazardous waste leachate. The sequential process configuration was chosen to minimize emission of volatile components present in the leachate. In the anaerobic process, 81% of the influent TOC (700–1000 mg/L) was removed. An additional 44% TOC removal was obtained in the aerobic reactor. 1,2 dichloroethane, ethylbenzene, methylene chloride, and phenol were removed to below detection limits in the anaerobic process. Significant removal of benzene, toluene, and bis (2-chloroethyl) ether also was achieved in the anaerobic process and only bis (2-chloroethyl) ether remained after aerobic treatment. Slonim et al. [10] assessed the removal of 4,6-dinitro-o-cresol (DNOC), a phenolic primary pollutant in a sequenced anaerobic/aerobic system. In the first stage anaerobic fixed-film reactor, DNOC was removed to below 1 mg/L using sucrose as a co-metabolite.
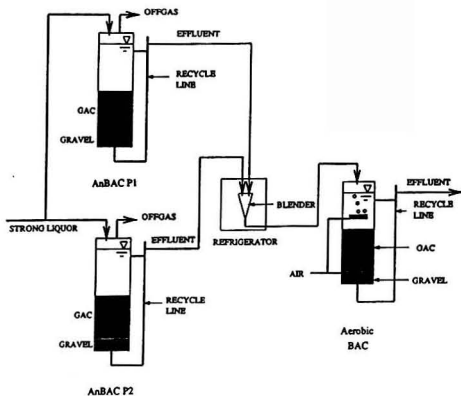
FIGURE 2. Schematic of sequenced pilot scale anaerobic/aerobic BAC columns.

The primary purpose of the second stage aerobic activated sludge reactor was to remove residual sucrose.

FACILITIES AND PROCEDURES

To assess sequenced anaerobic/aerobic BAC treatment of the OCC Durez strong liquor, effluent from two existing 17.8 cm ID pilot scale anaerobic biological activated carbon (AnBAC) columns was combined and fed to a single 15.2 cm ID aerobic pilot scale BAC unit which were located at the Durez facility. A schematic of the experimental units is presented in Figure 2. All effluent volume generated from the AnBAC columns was fed to the aerobic unit except for volume lost for AnBAC process effluent sampling. The purpose of this section is to provide details on the facilities and procedures employed to conduct these studies.

BAC Reactor Design

AnBAC Design

Two 17.8 cm ID plexiglass columns were employed for the pilot scale AnBAC studies. Each column had an empty bed volume of 30 liters and contained 8.5 kg of 8 × 16 mesh Calgon F-300 granular activated carbon (GAC). The carbon bed was maintained in an expanded mode by means of column effluent recycle. When not expanded, the carbon bed height was approximately 76 cm. Process off gas was measured using wet test gas meters. Full details of column construction are available in reference [11].

Aerobic BAC Design

The aerobic pilot scale BAC column was constructed of 15 cm ID acrylic tubing with total height of 130 cm. A 15.2 cm gravel layer was placed at the bottom of the column to support the carbon bed and provide for flow distribution. At the initiation of the aerobic BAC study, the column was charged with 2,200 g Calgon F-300 (8 × 16 mesh) GAC.

GAC bed expansion was achieved with a centrifugal recirculation pump. Initial expansion rate was controlled at approximately 30% of original bed height (35 cm). To provide for in-column aeration, four fine bubble air diffusers were evenly distributed at the bottom of carbon bed. Because of operational difficulties associated with this aeration option, namely carbon bridging and abrasion, a single 10 cm bar shaped

Table 1 COD and Phenols Concentrations of Strong Liquor During Study

Day of Operation	COD mg/L	Phenols mg/L
225–273	35,100	10,000
274–288	33,900	12,000
289–326	42,500	11,700
327–355	27,100	5,500

air diffuser was added above carbon bed to increase the oxygen transfer capacity.

Procedures

Pilot Scale AnBAC Studies

The feed strength for COD and phenols applied to the anaerobic columns during the study are presented in Table 1.

During these studies, the influent COD concentration of the strong liquor ranged from 42,500 to 27,100 and averaged 35,100 ± 4,100 mg/L based on a flow weighted average. Influent phenols concentrations during the same time ranged from 12,000 to 5,500 and averaged 9,830 ± 1,800 mg/L. A variety of macro and micro nutrients were added to the strong liquor to achieve a nutritionally balanced growth substrate. The composition of this feed solution has been presented previously [11].

Gas production and pH measurements for the AnBAC pilot scale facility were taken daily. Gas production volumes obtained from wet test gas meter recordings were corrected for STP. Periodically samples were taken from the off-gas for composition characterization. Samples for pH were taken from the column recycle lines. Samples for phenols and COD were taken twice weekly, or more often as required, from the recycle line as well. Because formaldehyde and methanol were not detected after anaerobic BAC treatment in earlier studies [11] they were not monitored during this study phase. Further details of AnBAC operation are available in reference [11].

Aerobic Pilot Scale BAC Operation

Effluent captured from the two pilot scale AnBAC columns were stored at 4°C and fed to the pilot scale aerobic BAC column without pretreatment. Influent samples for COD were taken on a daily basis from the feed tank which stored AnBAC effluent. Effluent samples for total and filterable COD were taken daily from the column recycle line. Samples for influent and effluent phenols, BOD$_5$, nitrogen, and suspended solids also were obtained from the recycle line. To minimize the biological activity in regions other than the carbon bed, the column side walls and recycle lines were cleaned regularly. The pilot scale aerobic BAC column was operated at room temperature 23 ± 1°C. Dissolved oxygen concentration in the column was measured daily and ranged from 5–7 mg/L.

The major components of the feed solution were metabolic end products of anaerobic biodegradation, anaerobic biomass sheared off from anaerobic columns, and phenol in relatively low concentrations. Because of the operating strategy employed for the first stage anaerobic BAC process there was significant variation in effluent composition. Influent total COD to the aerobic BAC process ranged from 5,144 to 601 and averaged 2,312 ± 1,050. Influent filterable COD ranged from 4,030 to 489 mg/L and averaged 1,800 ± 970 mg/L based on 54 observations. Influent phenols to the aerobic BAC process ranged from 0.02 to 461 mg/L and averaged 111 ± 61 based on 54 observations. Based on eight measurements, influent TSS and VSS concentrations to the aerobic BAC col-

FIGURE 3. AnBAC column PI effluent total COD and gas production during study period.
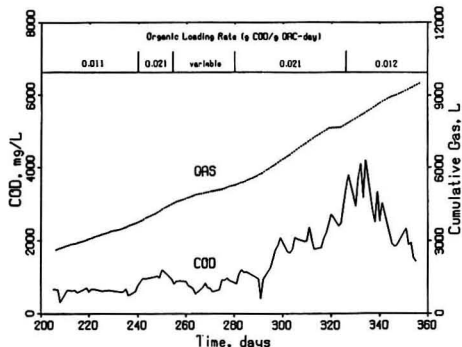
FIGURE 5. AnBAC column P2 effluent total COD and gas production during study period.

umn averaged 674 ± 295 mg/L and 436 ± 175 mg/L, respectively. In addition to fluctuations in AnBAC effluent quality, there also were variations in quantities of AnBAC column effluent. As a result, the influent flow rate to the aerobic BAC unit varied from 0 to 16 L/day with an average of 6.6 L/day.

Analytical Procedures

Analysis for COD was conducted in accordance with *Standard Methods* [*12*] Method 508B. Five day BODs were measured using *Standard Method* 507. Values reported for filterable COD and BOD5 correspond to the portion of material that passed through a Whatman GF/C filter. Phenols were measured according to *Standard Methods* S-510C (4-aminoantipyrine method). Total and volatile suspended solids concentrations were measured using *Standard Methods* S-209C and S-209D, respectively.

Composition of process AnBAC off-gas was measured with a Tracor 560 gas chromatograph equipped with a TCD, a 3.2 mm by 3.3 m stainless steel column with Carbosieve II 100/120 packing and a Perkin Elmer LCI-100 integrator.

RESULTS

AnBAC Column Results

Prior to their use in this study, the AnBAC columns were operated for 225 days as a stand alone system to assess the characteristics of AnBAC process operation. Results from this period of AnBAC column startup and performance have been presented earlier [*11*] and are not presented here.

Effluent total COD concentration, phenols, and cumulative gas production measured during this study for the two pilot scale AnBAC columns, designated P1 and P2, are provided graphically in Figures 3 and 4 for P1 and Figures 5 and 6 for P2, respectively. At the initiation of the sequenced anaerobic/aerobic BAC studies, Columns P1 and P2 were in a stable mode of operation with applied organic loading rates of 0.011 and 0.014 g COD/g GAC-d, respectively. During this stable period of operation, which started on day 206 and continued until day 240, effluent total COD averaged 632 ± 94 mg/L and 758 ± 147 mg/L for columns P1 and P2, respectively, based on 20 samples collected. Effluent COD concentrations reflect an average filterable COD removal efficiency of 98% for both columns. Based on 19 sampling dates effluent phenols averaged 0.39 ± 0.46 mg/L and 0.97 ± 0.83 mg/L for Columns P1 and P2, respectively during this period of stable operation. Column pH values were consistent for both columns and averaged 7.2. Production of biogas containing 75% methane was near stoichiometric expectations (0.35 L CH4/g COD) with actual ratios equal to 0.38 and 0.32 for Columns P1 and P2, respectively.

Because of apparent organic overloading and problems with strong liquor production the columns operated under variable conditions from day 241 to the end of the study. The highest effluent COD concentrations during this period were observed between day 330 and day 340 for Column P1 and on day 311 for Column P2 and resulted from organic overloading. Effluent phenol concentrations from P1 and P2 mirrored those of COD and were an important contributor to effluent COD concentrations during periods of high effluent COD. In Column P1, when effluent phenols approached 200 mg/L, gas production appeared to be affected adversely as indicated by a declining slope to the cumulative gas production curve pre-

FIGURE 4. AnBAC column PI effluent total phenols during study period.
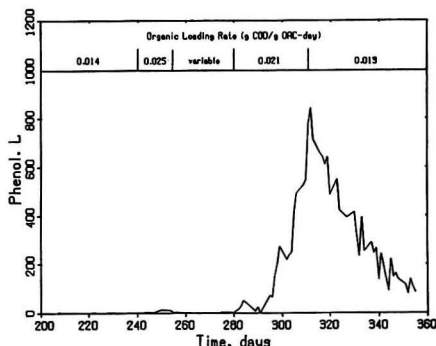
FIGURE 6. AnBAC column P2 effluent total phenols during study period.

Day of Operation	Column P1							Column P2						
	COD, mg/L		Solids, mg/L		VSS/TSS ratio	TSS yield	VSS yield	COD, mg/L		Solids, mg/L		VSS/TSS ratio	TSS yield	VSS yield
	inf	eff	TSS	VSS				inf	eff	TSS	VSS			
274	33,900	678	349	218	0.62	0.011	0.007	33,900	632	358	208	0.58	0.011	0.006
275	33,900	950	493	266	0.54	0.015	0.008	33,900	917	338	181	0.54	0.010	0.005
276	33,900	934	437	234	0.54	0.013	0.007	33,900	937	479	244	0.51	0.014	0.007
277	33,900	999	405	224	0.56	0.012	0.007	33,900	936	475	272	0.57	0.014	0.008
278	33,900	927	557	312	0.56	0.017	0.009	33,900						
281	33,900	839	493	284	0.58	0.015	0.009	33,900	1265	472	265	0.56	0.014	0.008
282	33,900	1094	339	179	0.53	0.010	0.005	33,900	1291	514	260	0.51	0.016	0.008
283	33,900	1222	422	242	0.57	0.013	0.007	33,900	1409	365	197	0.54	0.011	0.006
284	33,900	1146	335	230	0.69	0.010	0.007	33,900	1658	293	167	0.57	0.009	0.005
354	27,100	1882	627	431	0.69	0.025	0.017							
355	27,100	1948	617	435	0.71	0.025	0.018							

sented in Figure 3. The level portion of the cumulative gas production curve for P1 near day 325 in Figure 3 was due to a gas leak rather than inhibition. In Column P2, where reductions in gas production were more acute, peak phenol concentrations exceeded 800 mg/L. After this period of high phenols concentration in Column P2, the gas production rate remained low.

The inhibition of gas production resulting from phenol inhibition has been the focus of numerous studies. The concentration of phenol which results in 50% inhibition of methane formation has been found to range from 500 to 3,000 mg/L [13, 14]. Neufeld et al. [15] reported an inhibition constant equal to 966 mg/L phenol for an empirical model developed to express phenol toxicity. The form of the model closely resembled the Haldane Model [16]. Suidan et al. [17] determined the Haldane model constant K_i for phenol to be equal to 363 mg/L. Using these two inhibition constants as a guide, noticeable decreases in gas production would be expected at 800 mg/L phenol with less adverse affects apparent at 200 mg/L phenol, which is consistent with the data collected.

While gas production was retarded during periods of inhibition, the overall gas production rates for the two columns were quite consistent when averaged over the course of the study. For columns P1 and P2 from day 206 to day 357, the methane production ratios were 0.303 and 0.305 L CH$_4$/g COD removed. These values are close to the stoichiometric expectations. Accordingly, although there was significant inhibition of gas production at times during the study, these results suggest that the methanogen populations were capable of recovery.

Presented in Table 2 are influent and effluent COD concentrations and effluent TSS and VSS concentrations from the AnBAC Columns P1 and P2. Average observed yields for TSS and VSS were 0.014 g TSS/g COD removed and 0.008 g VSS/g COD removed. These average observed yield values are considerably lower than a value of 0.1 g VSS/g COD removed considered typical of anaerobic biological processes [18] and are reflective of the low system growth rates and long mean cell residence times which would be considered typical of the fixed-film AnBAC process. Wang et al. [19] in their studies with phenol treatment in AnBAC systems presented biomass yields ranging from below 0.001 to 0.007 mg VSS/mg COD. TSS and VSS yields for P1 were higher for the last two sample dates which occurred during a period of higher effluent COD. It is likely that the elevated COD concentrations promoted growth of bacteria in the bulk fluid. Increased biomass yields as a function of increased bulk fluid COD concentration also have been observed in aerobic BAC processes [20]. The volatile fraction of the effluent solids ranged from 51 to 71% with higher values calculated for periods of higher effluent COD. If as suggested above, the growth rate was increased during periods of high reactor COD concentration, it is not surprising

that the volatile fraction would be higher in these periods as well.

Aerobic BAC Column Results

Polishing of effluent from anaerobic pilot scale BAC reactors P1 and P2 in the aerobic pilot scale BAC column P3 was assessed for greater than 130 days of variable influent conditions. The assessment of the sequenced aerobic BAC process was conducted under variable influent conditions and provided a reasonable test of the buffering capacity of the aerobic polishing step. Parameters used to assess the polishing potential of the second stage aerobic BAC process included COD, phenol, BOD$_5$, and solids production.

Chemical Oxygen Demand

Presented in the top part of Figure 7 are the organic loading rates applied to the aerobic BAC unit. Organic loadings to the
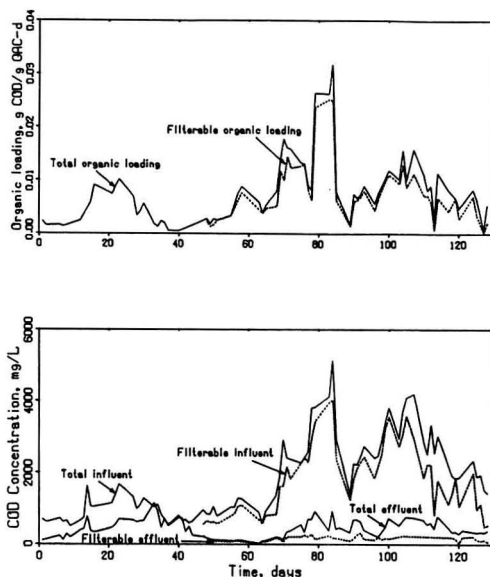
FIGURE 7. Influent COD loadings and influent and effluent COD concentrations in aerobic BAC column treating AnBAC treated strong liquor.
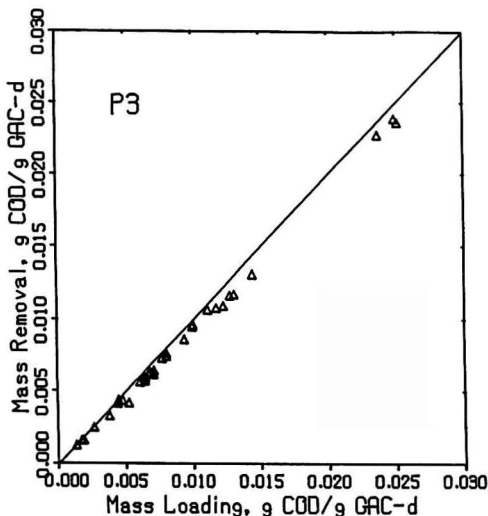
FIGURE 8. Filterable COD removal rate as a function of filterable COD loading rate.

aerobic pilot scale BAC process were variable. The highest organic loadings to the aerobic BAC process were achieved near day 80 of operation and resulted from organic overloading in the preceding AnBAC columns. For reference purposes, day 80 of aerobic pilot scale operation corresponds to day 309 of the AnBAC operation. During peak loading periods, daily total COD loading rates applied to the aerobic BAC reached as high as 0.032 g COD/g GAC-d. From day 48 to 131, the total and filterable COD loadings averaged 0.010 and 0.008 g COD/g GAC-d. These loadings represent relatively low organic loadings based on the treatment capacity of aerobic BAC process demonstrated in previous bench scale studies [20]. The non-filterable fraction of the COD loading was primarily cells sloughed during anaerobic treatment in Columns P1 and P2.

Influent and effluent COD concentrations measured during this period of operation are presented in the lower part of Figure 7. To give a more complete picture of process operation, filterable COD was measured in addition to total COD starting on day 48 of operation. From day 48 to day 131, the average effluent total and filterable COD concentrations were 405 ± 240 mg/L and 165 ± 82 mg/L, respectively. This compares to total and filterable influent COD concentrations of 2,312 ± 1,050 mg/L and 1,800 ± 970 mg/L, respectively, during the same time period. Using these averages, which were based on approximately 54 observations, 82% of the total COD and 91% of filterable COD applied during this period was removed in the aerobic BAC column.

In Figure 8, the daily COD removal rates recorded for filterable COD are plotted versus the influent filterable COD loading rate. The majority of applied loadings were in the range of 0 to 0.015 g COD/g GAC-d, although there were

several days when filterable COD loadings approached 0.025 g COD/g GAC-d. As evidenced by this graph and the effluent COD concentration data presented earlier, the pilot scale aerobic BAC process demonstrated a high level of treatment for all loadings applied and served as an effective polishing step despite fluctuations in the preceding AnBAC process.

Phenols and BOD₅

To assess the character of the effluent COD, effluent phenols and influent and effluent BOD_5 concentrations were monitored in the aerobic BAC column. Aerobic BAC effluent phenols measured for the aerobic pilot scale BAC process were very low throughout the study, averaged 0.04 ± 0.08 mg/L based on 27 measurements, and contributed little to effluent COD. Of these, 18 measurements were below or equal to 0.01 mg/L. The highest phenols concentration in the aerobic BAC effluent occurred on day 93 of operation was 0.34 mg/L.

To assess the biodegradability of the effluent COD, influent and effluent BOD_5 measurements were conducted on several dates with the results shown in Table 3. A high degree of filterable and total BOD_5 removal was achieved in the aerobic BAC process. Effluent filterable BOD_5 concentrations were low and represent almost complete conversion of filterable biodegradable organics in the BAC process. Effluent total BOD_5 were higher than filterable values and reflect the presence of effluent biological solids.

To further highlight the efficacy of the aerobic BAC process, filterable BOD_5/COD ratios were calculated for both influent and effluent samples. Based on the influent BOD_5/COD ratios, approximately half of the aerobic BAC influent organic loading was readily biodegradable. It is likely that the primary biodegradable components of the influent were volatile acids produced from primary substrate conversion in the AnBAC process and phenols not treated in the first stage anaerobic BAC process.

The low filterable BOD_5/COD ratio calculated for the effluent suggests that the majority of the effluent COD is non-biodegradable. If the averages for filterable influent COD to the first stage AnBAC process (35,000 mg/L) and filterable aerobic BAC effluent (165 mg/L) are compared, approximately 0.5% of the influent COD is discharged as non-bio-degradable COD. It is likely that this fraction is composed primarily of soluble metabolic endproducts (SMEP). Under normal biological process conditions, the fraction of influent COD discharged as SMEP ranges from 0.5 to 1.5% of the influent COD but can be much higher under very low and very high cell growth rates [21, 22, 23]. The 0.5% residual COD obtained in this study may be near the low range as a result of SMEP adsorption on activated carbon.

Solids Production

To assess the generation of biological solids in the aerobic pilot scale reactor, total and volatile solids were monitored on a limited basis during two separate occasions. Based on solids

Table 3 Influent and Effluent Filterable and Total BOD₅ and COD for Aerobic Pilot Scale BAC Column

Day of Operation	BOD₅, mg/L				COD, mg/L				Filterable BOD₅/COD	
	Filterable		Total		Filterable		Total			
	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff
70	787	4	1000	4	1645	75	2917	134	0.48	0.05
84	3425	13	3650	67	4030	176	5144	950	0.85	0.07
91	883	11	858	23	2128	268	2226	700	0.41	0.04
99	1562	2	1580	22	3243	174	3407	481	0.48	0.01
107	1625	3	1675	22	2980	—	4193	763	0.54	—

Day of Operation	COD Total, mg/L Inf	COD Total, mg/L Eff	COD Filterable, mg/L Inf	COD Filterable, mg/L Eff	TSS, mg/L Inf	TSS, mg/L Eff	TSS Y_T	TSS Y_F	VSS, mg/L Inf	VSS, mg/L Eff	VSS Y_T	VSS Y_F	VSS/TSS Inf	VSS/TSS Eff
54					1368	242			827	91			0.60	0.37
55	1065	108	812	65	556	218	-0.35	-0.45	330	66	-0.28	-0.35	0.59	0.30
56	1052	98	878	101	332	216	-0.12	-0.15	185	73	-0.12	-0.14	0.56	0.34
57	1304	126	1087	98	848	225	-0.53	-0.63	526	83	-0.38	-0.45	0.62	0.37
58	1284	119	1120	77	543	271	-0.23	-0.26	367	124	-0.21	-0.23	0.68	0.46
125	1882	327	980	127	627	1946	0.85	1.55	431	1096	0.43	0.78	0.69	0.56
126	1948	347	1144	101	617	2055	0.90	1.38	455	1213	0.47	0.73	0.73	0.59
127	1521	331	489	123	499	2138	1.40	4.48	370	1168	0.67	2.18	0.74	0.55

Y_T = solids yield resulting from utilization of total COD
Y_F = solids yield resulting from utilization of filterable COD

and filterable COD data in Table 4, negative solids yields were observed in the first data reporting period while yields greater than 1 mg VSS/mg COD removed were observed in the second reporting period. Negative solids production suggests that, although there was solids production from aerobic conversion of influent organics, the degradation of anaerobic biomass loaded to the aerobic BAC column was greater than the production rate. The higher yields observed during the second period, however, are not sustainable for long periods of operation and may be the result of excessive shear of attached biofilm and/or utilization of previously adsorbed organics during this period. Given the low effluent concentration of filterable COD achieved in the column throughout the study, shear loss seems a more likely explanation.

While the lack of sufficient VSS and TSS data make definitive conclusions regarding the system yield data impossible, of the two data periods, the first data collection period is considered more representative of eventual process operating conditions. In previous aerobic bench scale studies [20], VSS yields were found to be a function of organic loading and averaged 0.05 mg VSS/mg COD at an organic loading rate of 0.02 g COD/g GAC-d. During both reporting periods used for yield calculations, the organic loading rate varied between 0.005 and 0.01 g COD/g GAC-d. At these lower organic loadings, VSS yields lower than 0.05 mg VSS/mg COD would be expected. A reduction of the effluent VSS/TSS ratio relative to the influent would also be expected at these lower organic loading rates as observed.

SUMMARY

Based on the results of this investigation, sequenced anaerobic/aerobic BAC process treatment of the strong liquor produced at the Occidental Chemical Corporation's Durez Division is feasible and can achieve a high quality effluent. As concep-

tualized, the first stage anaerobic BAC process achieves significant organic conversion with minimal solids production and appreciable methane production. Excellent polishing of the AnBAC process effluent is achieved in the aerobic BAC unit even under variable influent conditions. Effluent filterable COD from the aerobic BAC process averaged 165 mg/L and was speculated to be primarily non-biodegradable soluble metabolic endproducts. Effluent phenols from the process often were below 0.01 mg/L and averaged 0.04 mg/L.

Projected effluent quality of the sequenced process calculated based on the data gathered in this study is presented in Table 5. For the purposes of these calculations it was assumed that the influent COD and phenols were equal to 35,000 mg/L and 10,000 mg/L, respectively. Given the nature of these estimates, concentration values were rounded to the nearest 50 mg/L value where appropriate.

Effluent filterable COD from the AnBAC process is expected to vary from 750 to 1,000 mg/L under non-inhibitory organic loadings. After aerobic polishing, an effluent with approximately 150 to 200 mg/L filterable COD with little oxygen demand is expected. Effluent phenols from the AnBAC process are expected to be consistently below 5 mg/L and average 1 mg/L. In the subsequent aerobic BAC reactor, phenols would be reduced further to below 0.05 mg/L. If the gas production rate varies between stoichiometric predictions and 0.30 L CH$_4$/g COD removed, which was the long term average over the course of this study, approximately 10 to 12 L CH$_4$/L of strong liquor treated would be produced.

Assuming an AnBAC biomass yield ranging from 0.01 to 0.02 mg VSS/mg COD removed, effluent VSS concentrations from the AnBAC process would range from approximately 350 to 700 mg/L. Effluent TSS concentrations would range from approximately 600 to 1,150 mg/L TSS if a VSS/TSS ratio of 0.60 is operative. If endogenous decay in the subsequent aerobic BAC is neglected, and an aerobic BAC yield of 0.05 mg VSS/mg COD was operative, an effluent VSS con-

Table 5 Projected Effluent Concentrations for AnBAC and Aerobic BAC Processes When Treating Strong Liquor

Constituent	Influent[a] mg/L	AnBAC Effluent Conc Range mg/L	AnBAC Effluent Rem %	Aerobic BAC Eff. Conc. Range mg/L	Aerobic BAC Eff. Rem %	Overall Removal %
Fil. COD	35,000	750–1000	>97	150–200	>80	>99
Total COD	35,000	1100–1700	>95	550–950	50	>97
Phenols	10,000	<5	>99.9	<0.05	>99	≈100
Methane	0	10–12[b]				
VSS	0	350–700		400–750		
TSS	0	600–1150		1200–2300		

[a] a typical characterization assumed for the strong liquor
[b] L CH$_4$/L strong liquor treated

centration of ranging from approximately 400 to 750 would be realized from the aerobic BAC polishing reactor. If these solids were assumed to have an oxygen demand equivalent of 1 mg O_2/mg VSS, then the total COD from the anaerobic and aerobic BAC units would range from approximately 1,100 to 1,700 mg/L and 550 to 950 mg/L, respectively.

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Bioremediation: An Effective Remedial Alternative for Petroleum Hydrocarbon-Contaminated Soil

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Bioremediation technologies applied to contaminated soil usually mitigate environmental rate-limiting factors so that biodegradation rates are maximized for any given compound. A newer approach to soil bioremediation mitigates these environmental rate-limiting factors simultaneously, initially allowing biodegradation to proceed at a maximal rate without the need for additional action. This technology involves intensive mixing of contaminated soil in a ribbon blender, introduction of a protein-based, surfactant-containing nutrient additive to the soil while in the mixer, physical entrainment of oxygen-containing air into the soil, discharge of the mixed soil from the mixer, and placement of the mixed soil in curing piles, for curing, during which time biodegradation can occur. No additional treatment actions (e.g., tillage, fertilizer or water applications) are typically required. The remediation, using this approach, of a former distribution facility which possessed soil contaminated with gasoline, is summarized.

INTRODUCTION

Bioremediation applications all employ the use of microorganisms, both bacteria and fungi, to biologically oxidize organic contaminants present in various contaminated media. Bioremediation techniques exploit the abilities of these organisms to oxidize various organic compounds biochemically. The endproducts of contaminant oxidation are typically CO_2 and additional bacterial biomass. Bioremediation has been previously applied to all types of contaminated media, including air, using bioventing [1], to contaminated groundwater [2], to sludges [3] and to soils [4, 5]. Considering the amount of contaminated soil present both in the U.S. and abroad, it is clear that bioremediation of contaminated soils offers a cost-competitive, contaminant-destructive remedy for many sites currently faced with costly incineration or the extended liability of landfilling.

It is well established that microorganisms, chiefly bacteria,

are capable of mediating biodegradation of a wide variety of compounds, including aliphatic and aromatic alkanes comprising petroleum fuels [6, 7], PAHs [7], chlorinated aliphatic hydrocarbons, such as TCE [8], and even chlorinated aromatics such as PCP [9, 10] and PCBs [11]. However, most field applications of bioremediation technologies have been to soil that is contaminated with petroleum products. This is primarily due to the fact that soil bacteria are quite adept at degrading the individual hydrocarbon constituents (i.e., alkanes and aromatics) that comprise petroleum products. Furthermore, it is well established that these compounds are biodegradable, in the laboratory, in pure and mixed cultures [6, 12], in the laboratory, in soil microcosms [13, 14], and in the field under conditions of full-scale site remediation [4, 15]. Much is known about the biochemistry of hydrocarbon degradation, and the biochemical pathways employed for degradation are well established. Furthermore, many bacterial species are capable of mediating degradation of hydrocarbon compounds, and their distribution in nature is wide.

There are several methods of soil bioremediation that have been successfully employed. These include the more traditional

ex-situ approaches, such as landfarming [5] and composting [16], to more advanced applications, such as bioreactors [17]. *In-situ* systems have also been employed with success on many sites where excavation is not desired [18].

One key factor that all effective soil bioremediation applications share is that the application design must effectively compensate for the rate-limiting effects of various parameters, both microbiological and environmental.

RATE-LIMITING FACTORS FOR SOIL BIORE-MEDIATION APPLICATIONS

Although it is well established that petroleum hydrocarbon compounds will be biologically degraded under optimal environmental conditions, frequently, in natural environments, such as soil ecosystems, environmental and other parameters may limit biodegradation rate of the contaminants of interest such that bioremediation is not a feasible option for site remediation. In many cases, preliminary laboratory studies have yielded effective biodegradation rates because environmental conditions were easily controlled in a laboratory setting. However, when these applications scaled up to the field level, frequently, substantially different contaminant removal rates were observed in the field relative to those observed in the laboratory. This is largely due to a failure of the application to fully account for the various rate-limiting factors prevalent in soil systems.

Rate-limiting factors for field applications of bioremediation technologies can be classified according to two principal sources:

* Those that are biochemical and microbiological; and
* Those that are environmental

Various rate-limiting factors are discussed at length below.

Biochemical/Microbiological Rate-Limiting Factors

Microbiological and biochemical limiting factors are the most direct limiting factors for the bacterial biodegradation rate of hydrocarbon compounds and these are also the hardest to effectively mitigate by engineering techniques. The principal rate-limiting factor for soil bioremediation applications in this regard is the absence of a bacterial population or species that is capable of degrading hydrocarbon compounds. Because hydrocarbon-degrading bacterial species are ubiquitous in nature, it is highly unlikely that any soil system would be deficient in such bacteria. On one site, it was shown that addition of acclimated bacteria (bioaugmentation) to petroleum contaminated soil did not significantly change the biodegradation rate for these compounds [5]. This observation tends to imply that bacteria capable of hydrocarbon degradation were already present in soil from this site in sufficient number to carry out effective biological degradation of hydrocarbon compounds. However, there is a controversy as to the effectiveness of bioaugmentation practices. These conflicting results are discussed at length by Atlas [19].

Environmental Rate-Limiting Factors

While optimized environmental conditions can be easily maintained in the laboratory, in the field, environmental conditions are rarely optimized. There are a number of environmental rate-limiting factors associated with soils that can profoundly change the organic compound biodegradation rate. These parameters include:

* Temperature
* Oxygen Supply
* Nutrient Status

* Contaminant Bioavailability/Soil Chemistry
* Contaminant Chemical Structure
* Population Ecology

Temperature affects biodegradation applications in two ways. Both the specific growth rate of the degrading microorganisms and the activity of the enzymes responsible for contaminant oxidation are largely temperature dependent, rapidly decreasing in response to temperature drops. It has been determined that for most soil contaminated with most petroleum products, the temperature that provided optimal growth rates was 27°C [13]. Lower temperatures will cause lower biodegradation rates, but biodegradation will still occur to some extent. When the freezing point of water is reached, biological activity with regard to hydrocarbon biodegradation halts. Some bioremediation designs have incorporated methods by which an optimal temperature can be maintained in the field. Some of these methods include covering exposed soil with black plastic to retain heat within the soil mass and the construction of a heated enclosure so that a constant soil temperature can be obtained. The latter method is best suited to small quantities of soil, for economic reasons.

Hydrocarbon compounds can be biologically degraded either aerobically (using oxygen) or anaerobically (in the absence of oxygen). The most effective biodegradation of hydrocarbon compounds is mediated aerobically, by aerobic bacteria. This is largely due to the greater energy yielding capacity of aerobic respiration relative to both anaerobic respiration and fermentation. Soil oxygen content is frequently a rate-limiting factor for many high rate bioremediation applications [20]. In order to mitigate the potential for rate limitation due to oxygen deficiency, most soil bioremediation applications include the delivery of oxygen in their design. Tillage, air injection systems, and the addition of hydrogen peroxide have all been used for this purpose.

Nutrient concentration is another critical factor to consider when bioremediation technologies are applied to contaminated soil in the field. In most soil systems, organic carbon is rarely present in growth-limiting concentrations. Nitrogen and phosphorus, two inorganic nutrients critical to bacterial growth, are frequently present in soil systems in insufficient quantities to allow for both high rates of bacterial growth and high rates of organic compound biodegradation. Consequently, most bioremediation applications incorporate the addition to these nutrients in their design.

The biological availability of the contaminant(s) of interest to soil bacteria can frequently be a rate-limiting factor with regard to biodegradation of these contaminants. The biological availability of petroleum hydrocarbons is an index of the ability of soil microflora to come into contact with, and subsequently degrade, petroleum hydrocarbon compounds. This parameter is largely a function of soil chemistry. In many soil systems, contaminants may be unavailable due to contaminant hydrophobicity, sorption onto the soil colloid, volatilization potential, or dissolution into soil organic matter. Of these, the two predominant causes for the lack of contaminant bioavailability are usually contaminant hydrophobicity and the potential for volatilization. Many bioremediation systems incorporate a mechanism to make contaminants more biologically available in their design. These have included the inclusion of a surfactant in the treatment train and intensive mixing to increase the mass transfer of contaminants to an aqueous phase, typically accomplished either by tillage (landfarming) or mechanically (bioreactors).

Contaminant chemical structure is also a major factor governing the biodegradation rate for a mixed molecular weight contaminant, such as petroleum fuels. As a general rule, the more complex an organic compound, the more difficult that compound is to biologically degrade. Therefore, longer periods of time are typically required for heavier molecular weight compounds, such as the alkanes comprising oil, relative to the lighter molecular weight compounds, such as the alkanes com-

prising gasoline. A similar statement can be made for the degree of branching present within the carbon chain of the compound under consideration. For example, tertiary alkanes and alcohols are more recalcitrant than are secondary alkanes and alcohols, which are more recalcitrant than are *n*-alkanes and alcohols. For this reason, differential rates are observed when considering the biodegradation of various molecular weight fuels, which are comprised of different proportions of each compound. It has been shown, at the bench scale, that the length of time required to treat soils contaminated with gasoline, jet fuel, heating oil, diesel oil, and bunker C using bioremediation increased as a function of the carbon chain length of the principal contaminants, with the order of persistence being bunker C > diesel oil > heating oil > jet fuel > gasoline [13]. A similar statement can also be made for polyaromatic hydrocarbons (PAHs). Typically, heavy weight, higher order PAHs (e.g., benzo(a)pyrene, indeno(1,2,3-cd)pyrene, etc.) are more recalcitrant than are lighter molecular weight PAHs (e.g., naphthalene, α-methyl naphthalene, etc.), and as such require longer time frames for equivalent degradation to occur [21].

Soil population ecology can also be a rate-limiting factor with regard to biodegradation of petroleum hydrocarbon compounds. In most soil ecosystems, petroleum fuels are degraded commensally, with different bacterial populations actually degrading the different types of compounds present in petroleum fuels. This phenomenon has been demonstrated by Compeau and colleagues [5]. Hydrocarbon-degrading bacterial populations must compete with non-hydrogen utilizing bacteria for available nitrogen and phosphorus, oxygen, water, and space. Thus, a natural limit exists on the maximum population density of hydrocarbon-degrading bacteria that is achievable in any soil system. Furthermore, natural bacterial predators, such as protozoa, feed on soil bacteria nondiscriminantly, so that total heterotrophic and hydrocarbon-degrading bacterial species are reduced in number. There is very little that can be done to mitigate the effects of competition and predation in soil ecosystems.

THE SAFESOIL℠ BIOTREATMENT SYSTEM

A new approach to the more classical bioremediation applications involves excavation and powerscreening of contaminated soil. The screened soil is then transported to a ribbon blender, where it is mixed with a combination of protein, surfactants, inorganic nitrogen and phosphoros salts and water. Air is physically entrained into the soil during this step of the treatment train. The mixed soil is then placed in "curing" piles on site for the "curing" portion of the treatment process, during which time biodegradation by microorganisms (bacteria and fungi) will occur.

In contrast to most other *ex-situ* bioremediation technologies, this technique does not require any further soil processing. All nutrients that are required are supplied during initial processing. The unique air entrainment feature of the treatment process provides an initial supply of oxygen and provides for passive air diffusion, by the generation of a honeycomb lattice structure, which prevents oxygen from becoming limiting.

A conceptualized mechanism for enhanced bioremediation of petroleum hydrocarbons using this technology is that the surfactant properties of the additive enable it to emulsify short chain volatile hydrocarbons, suppress volatilization, solubilize long chain hydrophobic contaminants, thus making them available for biodegradation, and mobilize adsorbed microbial cells and contaminants. Inorganic nutrients, principally nitrogen and phosphorus, present in the additive to stimulate growth of natural microorganisms. Furthermore, the additive contains simple sugars and readily utilizable organic C sources (primarily single sugars and protein) to increase the indigenous

microbial population size to a level able to rapidly oxidize organic compounds. During the curing portion of this process, microbial (primarily bacterial) cells, stimulated by these inorganic and organic nutrients grow and, in the process of growth, degrade contaminants. The growth of these microbial populations is allowed by aerobic conditions maintained throughout the curing pile during curing.

PROJECT SUMMARY

A representative project is summarized as follows:

Site History

A former distribution facility in Tustin, California, experienced soil contamination from nine leaking underground storage tanks. The only petroleum contaminant present was gasoline. Over 8,900 cubic yards of gasoline-contaminated soil was excavated and treated on site. Soils encountered during this project included clays and sandy clays. The treated material was backfilled on site following achievement of action levels. Project action levels were 50 ppm TPH, 0.1 ppm benzene, 0.1 ppm toluene, 0.3 ppm ethylbenzene, and 0.3 ppm xylene. TPH was measured by EPA Method 8015, while BTEX was measured by EPA Method 8020.

The stockpiled, contaminated soil was thoroughly characterized with respect to the concentrations of gasoline-derived total petroleum hydrocarbons (TPH), benzene, toluene, ethylbenzene, and xylene. Pretreatment TPH concentrations ranged from 85 to 8,900 ppm, with the bulk (approximately 90%) of the treated material possessing TPH concentrations of <3,000 ppm (see Figure 1). The average pretreatment TPH concentration was 1,296 ppm. Pretreatment benzene concentrations were less pronounced, ranging from 0.3 to 52 ppm. The bulk of the stockpiled material (approximately 85%) possessed benzene contamination levels of <3 ppm (data not shown). The average benzene pretreatment concentration was 2.6 ppm. Pretreatment toluene concentrations ranged from 0.3–290 ppm (data not shown), with 90% of the stockpiled soil possessing a toluene concentration of 75 ppm or less. Pretreatment soil ethylbenzene concentrations ranged from 0.4–50 ppm, with an average concentration of 4.5 ppm (data not shown). Xylene was the most prevalent of the aromatic contaminants under consideration. Pretreatment xylene (as total xylenes) concentrations ranged from 0.8–500 ppm; the bulk (90%) of the stockpiled soil possessed xylene contamination of <200 ppm (data not shown). The mean pretreatment soil xylene concentration was 71 ppm.

Soil contaminant levels were such that biological treatment is a viable option. The concentration of lipophilic compounds, primarily BTEX and higher molecular weight alkanes, was not sufficiently high to cause bacterial inhibition. Similarly, pre-
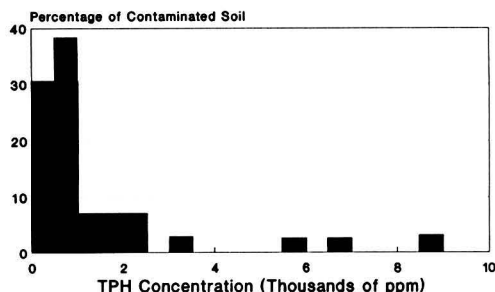
FIGURE 1. Contaminated soil pretreatment TPH concentrations (Tustin project).
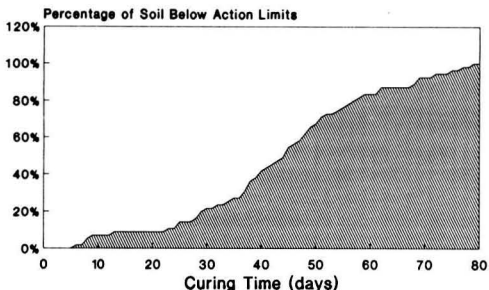
FIGURE 2. Cumulative relative frequency distribution for TPH curing time (Tustin project).

FIGURE 4. On-site testing results (Tustin project).

treatment concentrations of these compounds were not below the threshold concentration for biological degradation to occur.

Performance Data

This technology was effective at mediating the removal of both the total petroleum hydrocarbons (TPH), and monoaromatic hydrocarbons (BTEX) to below the action limits for 100% of the treated soil. A relative frequency distribution for curing time is presented in Figure 2 for gasoline-derived TPH and in Figure 3 for BTEX. The median posttreatment curing times for both TPH and BTEX biodegradation were 43 and 45 days, after which time approximately 40% of the soil had been remedied to below action limits for both the TPH constituents of gasoline and BTEX. All of the soil was treated to below action limits for both TPH within 80 days curing time (see Figure 2) and for BTEX within 78 days (see Figure 3).

On-Site Testing

On-site testing was initiated to determine the rate of TPH and BTEX biodegradation, as well as to measure changes in bacterial biomass as a function of time. These data are summarized in Figure 4. Briefly, the data show that soil contaminated with gasoline-derived TPH in the 800–1000 range could be remedied to below the action limit in an anticipated time frame of 35–45 days posttreatment. This is consistent with the observed median curing time for TPH (see Figure 2). Soil bacteria were also monitored as a function of posttreatment curing time, and these data are also summarized in Figure 4. Soil bacterial biomass increased 100 fold in response to treatment, and then declined to near pretreatment levels by day 27–30 (see Figure 4). The observed rise and decline of bacterial biomass is coincident with median time frame for TPH/BTEX
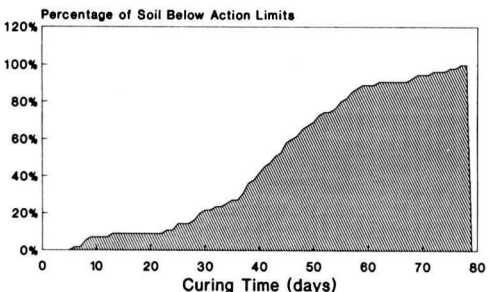
FIGURE 3. Cumulative relative frequency distribution for BTEX curing time (Tustin project).
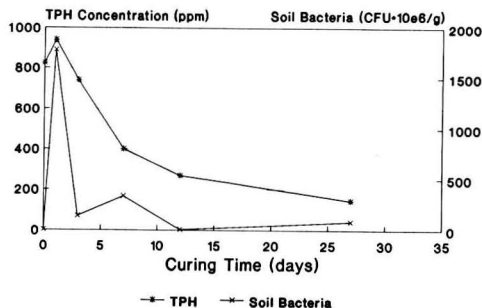
removal for this project, and implies that the observed TPH/BTEX removal was mediated biologically, chiefly by bacteria.

Volatilization Measurements

It was hypothesized, based on VOC monitoring data for another, similarly contaminated site [4] that volatilization only accounted for a minor portion of contaminant removal. To confirm this premise, a mass balance was performed to quantify the amount of gasoline-derived hydrocarbons removed by volatilization as a consequence of treatment using this technology. This analysis involved trapping evolved gas from the excavated soil at various points during the treatment train: stockpiling/handling, mixing, and curing.

The protocol employed to quantify VOC release is summarized below. To quantify VOC emitted during the stockpiling/handling portion of the process, the gas emitted was trapped by placing a cone of known volume and conical base surface area over the surface of the soil in the front-end loader en route to the mixer from the stockpile. The gas phase was allowed to equilibrate, and when equilibrium had been reached, the gas phase was purged and trapped in a Tedlar bag. The contents of this bag were analyzed by capillary gas chromatography to determine the identity, molecular weight, and concentration of each individual constituent comprising gasoline that evolved from the soil due to soil movement. To quantify the VOC emitted during mixing, the gas stream emitted from the mixer was trapped in a Tedlar bag and analyzed by capillary gas chromatography. This procedure was followed for this gas stream prior to passage through a carbon adsorption unit (pollution control system) and the gas emitted from the carbon adsorption canisters was monitored for VOC concentration using an OVA. This allowed for quantification of the amount of the hydrocarbon compounds removed from the soil, by weight, by volatilization and the amount of VOC by weight actually emitted to the atmosphere. The VOC emitted to the atmosphere during curing were quantified by a method similar to that used to quantify VOC emitted during soil stockpiling and handling, except that VOC emissions were calculated from the curing pile at various points in time rather than from the front-end loader.

The data for this analysis are summarized in Figures 5 and 6 and are expressed on a proportional basis. The soil on which VOC measurements were made was characterized intensively ($n = 5$ samples) to determine its pretreatment TPH concentration and the weight of the soil batch under consideration. Soil TPH and BTEX concentrations were also measured as a function of time to quantify the amount of gasoline weight hydrocarbon compounds removed over the course of time. The proportion of these compounds removed by volatilization is defined as the weight of the hydrocarbon compounds volatilized divided by the total hydrocarbon weight removed. Nonvolatile contaminant removal, predominantly biodegra-

Nonvolatile Contaminant Removal 99.0%

Trapped 73%

Released 27%

Volatilization 1.0%

Note: Values expressed as a percentage of the total amount removed
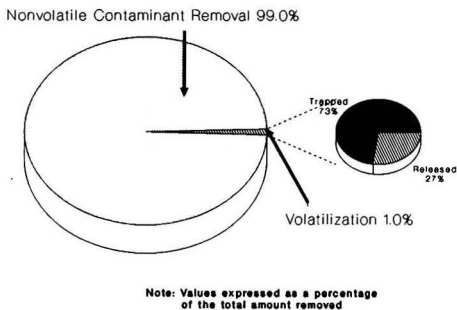
FIGURE 5. Removal sources for volatile organic compounds (Tustin project).

dation, accounted for the removal of 99%, by weight, of the gasoline hydrocarbon compounds initially present in the stockpiled soil, while volatilization only accounted for 1% of this amount (see Figure 5). And, only 27% of the 1% volatilized was released to the atmosphere; the remainder was trapped on the carbon adsorption component of the pollution control system and not released to the atmosphere (see Figure 5). The mixing component of the SafeSoil process accounted for roughly 96% of the contaminants lost from the soil by volatilization, while soil handling resulted in a loss of 3.7% and curing resulted in a loss of only 0.3% of the contaminants under consideration (see Figure 6). This was to be expected, owing to the instantaneous increases in soil porosity and surface area caused by mixing. The data clearly demonstrate that nonvolatile contaminant removal (principally biodegradation), and not volatilization, was the chief removal mechanism for the treated soil, accounting for removal of approximately 99%, by weight, of the contaminants present for this project.

SUMMARY AND CONCLUSIONS

The data suggest that the strategies employed to mitigate environmental rate-limiting factors incorporated into the design of the SafeSoil application are effective. This technology was demonstrated to be effective at stimulating biodegradation of gasoline in soil, with only a small proportion (1%) of the gasoline-weight hydrocarbons present in the soil being removed by volatilization. The only rate-limiting factors not effectively mitigated by this technology are temperature and population ecology-derived factors (e.g., predation and nutrient competition among non-degrading bacterial species). Mitigation strategies for these specific rate-limiting factors are an area of bioremediation research and development that has received considerably less attention than have mitigation strategies for

Mixing 95.92

Curing 0.32
Handling 3.76

Note: Values are expressed as a percentage of the total amount volatilized
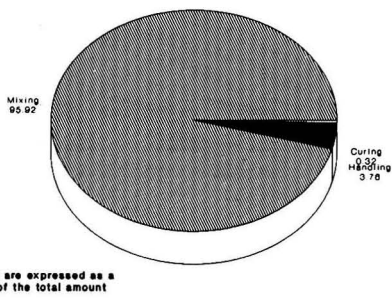
FIGURE 6. Emission Sources for VOC release (Tustin project).

other rate-limiting factors. It is important to realize that these rate-limiting factors are based on trophic interactions between numerous groups of microorganisms (protozoa, hydrocarbon degrading and non-hydrocarbon-degrading bacteria) that have evolved over time. Techniques for exogenous manipulation of microbial trophic dynamics are therefore one of the most promising avenues to improve speed and performance in bioremediation applications.

Comparison of data generated from the current project with data collected during other field applications of this technology [4, 22] indicate that biodegradation rates are quite variable. This variance is largely site-specific, depending on a number of factors, including the type and concentration of the contaminants of interest, and the indigenous bacterial population type and size. Regardless of site-specific variances in biodegradation rates, bioremediation remains a viable remediation technique for petroleum-contaminated soils.

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Effects of Fine Powder Addition on the Sludge Unit of a Chemical Wastewater

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Equilibrium powdered activated carbon (PAC) concentrations of 20, 160, and 280 mg/L in bench-scale activated sludge units treating cellulose acetate processing wastewater were found to enhance substrate removal. The mean improved COD removal was 20 percent. The apparent mechanism of enhanced substrate removal was the stimulation of greater biomass growth.

PAC addition increased the oxygen uptake rate (OUR), the observed cell yield coefficient (Y_{obs}) and the pseudo-first order substrate removal coefficient (K_b), of the activated sludge system, which was operated at a temperature of 18°C and at a mean cell residence time (MCRT) of 14 days. The addition of PAC also improved the sludge settleability, but this resulted in higher effluent SS concentration because zone settling velocity (ZSV) was the primary factor affecting effluent SS.

INTRODUCTION

Increasing popularity in biofilm systems may render the existing activated sludge systems treating chemical wastewaters obsolete as industries seek to meet the stringent effluent limitations. This arises from the fact that chemical wastewaters are usually laden with toxic organic compounds and with recalcitrant organics to biodegradation. As a sequel, there is a resurgence of interests in the application of some form of biocarrier material in the activated sludge process.

One such application is the addition of powdered activated carbon (PAC) to the aeration vessel of the activated sludge (AS) Process, commonly termed the PACT Process. The PACT Process can be regarded as a completely mixed biofilm and biofloc system, and its performance could to some extent approximate that of a typical biofilm system. In the presence of a carbon type, there would be a "complete" degradation of the organics. This stems from the fact that the carbon detention time would equal the operating system's mean cell residence time (MCRT). Consequently, the detention time of the adsorbed organics would no longer be the same as the system's hydraulic residence time (HRT) but equals the operating MCRT. This condition gives the microorganisms enough time to completely degrade the organics if all the necessary specific enzymes for its decomposition are present in the microbial mass.

The merits of the PACT Process are thoroughly documented in the existing literature [1, 2, 5-11, 13, 14]. Regardless, wastewater characteristics differ from industry to industry. There can even be a substantial variation in wastewater characteristics in a particular industry. The PACT process is mainly amenable to wastewaters containing adsorbable toxic and poorly biodegradable organics [1, 2, 11]. However, the chemical wastewater in question contains highly biodegradable but poorly adsorbable organics, some of which are thought to be toxic. Literature reported that AS and PACT processes sequester rapidly biodegradable organics in equal amount [2, 6]. The benefits of PACT for treatment of a highly biodegradable but poorly adsorbable organic wastewater are, therefore, in doubt.

There are three basic schools of thought on the mechanism of enhanced substrate removal [11, 13, 16, 18, 19]: physical adsorption, combination of biodegradation and physical adsorption, bioactivity and bioregeneration. This study was, however, directed at elucidating the performance characteristics of the activated sludge unit of an industrial cellulose acetate resin (cellar) processing wastewater on the addition of PAC. The specific objectives were:

- To evaluate the enhancement of substrate removal by the addition of PAC to the sludge unit of cellar wastewater.
- To determine the cardinal mechanism of improved substrate removal by PAC in the activated sludge process.

- To establish the relationship among PAC, sludge settleability and effluent suspended solids.
- To evaluate the effects of PAC on the pseudo-first order kinetic constant, and the stoichiometric observed yield parameter of the activated sludge process.

EXPERIMENTAL PROCEDURES

Experimental Equipment and Wastewater Composition

Two laboratory scale, continuous-flow reactors with internal recycle were operated in parallel. One reactor contained PAC and the other a control unit without PAC. The Monostat Cassette pump head, in addition to gravity, was used to pump the influent wastewater from the carboy to the reactors.

Wastewater was sampled at the effluent point of equalization basin of the cellar treatment system where the pH was typically 4.6. The wastewater sampled at this point represented the feed wastewater components of the aeration basin. Because the inlet pH was around the pk_a of CH_3COOH, the major component of the wastewater was acetic acid, with other constituents such as mesityl oxide (MeO), diisobutyl ketone (DIBK), methyl cyanide (CH_3CN), methylethyl ketone (MEK), and benzene. The wastewater was stored at 4°C, and each batch of the wastewater was stored for a maximum of one week. It was assumed in this study that COD lost due to storage and transport was negligible.

Experimental Approach

The mixed liquor suspended solids (MLSS) of the wastewater treatment plant was utilized to start up the bench-scale reactors. The inlet wastewater was set at 4.32 liters per day. The total volume of each reactor was 16.5 liters, which gave a hydraulic residence time of 3.8 days. The feed lines were changed every two weeks to prevent bacteria from growing in the inlet wastewater source. The two bench-scale heterogeneous culture, continuous-flow completely mixed activated sludge when then operated at a mean cell residence time (MCRT) of fourteen days at an average temperature of 18°C. The daily effluent suspended solids were determined for each unit to maintain MCRT constant. This assisted also in calculating the amount of daily wasting necessary for each bioreactor.

The bioreactors were operated to steady states as measured by COD, specific oxygen utilization rate (SPOUR), and MLVSS before PAC addition was begun. Each time an equilibrium carbon concentration was established in the bioreactor, it was allowed to reach a steady state, and data were collected over the steady state period. Other investigational parameters monitored were DO, TOC, pH, OUR, SVI and ZSV. The inlet COD was unfiltered while the outlet COD and/or TOC were filtered through 5.50 diameter, 1.5 μm Whatman filter paper. The filtrate was then filtered with 0.45 μm filter paper to remove all bacteria. All tests were performed according to Standard Methods for the Examination of Water and Wastewater [20].

At the end of the day, the effluents in the carboys were emptied. In other words, the effluents in the carboys represented a 24-hour composite sample. The feed wastewater constituents were determined on grab bases while the effluents were composite samples. The inlet volumetric flow rate was checked and/or adjusted twice daily. The addition or replacement of PAC was the last operation in each day.

Addition of PAC to the Bioreactor

A carbon type, sorbonorit 3B, was used in the experiment. The sorbonorit was blended with an electric blender and dried at a constant temperature of 103°C. It was sieved and the
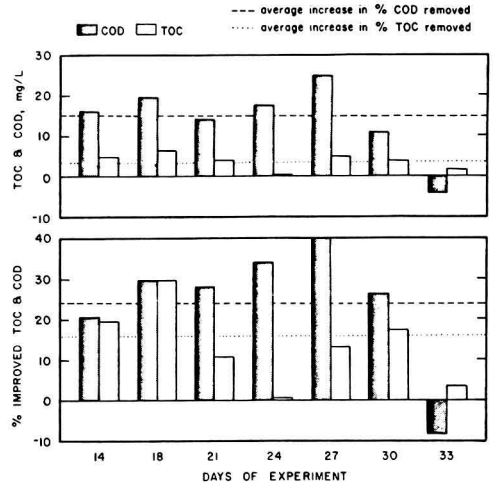
FIGURE 1. Improvement in substrate removals by the PAC unit at an equilibrium PAC concentration of 280 mg/L.

particle size that was retained on sieve no. 300, but passes through sieve no. 200, was used in the test. The mean diameter of the particles was determined to be 0.0056 cm.

The initial PAC concentration added to the reactor was 20 mg/L. This amount was added daily for fourteen days, and the concentration of PAC built up to 280 mg/L. The PAC was added daily and wasted as a function of MCRT. This equilibrium concentration was maintained in the reactor by wasting and replacing the amount until steady state was reached as measured by MLSS and COD. Following the 280 mg/L experiment, a new equilibrium concentration of 160 mg/L was established by wasting daily without replacement. Similarly, 160 mg/L of PAC was reduced to 20 mg/L. Thus, the three experiments were performed at mixed liquor carbon concentrations of 280, 160, and 20 mg/L.

RESULTS AND DISCUSSION

Substrate Removal

The units with PAC showed better substrate removals for all the trial runs. Figures 1, 2, and 3 depict the results of the
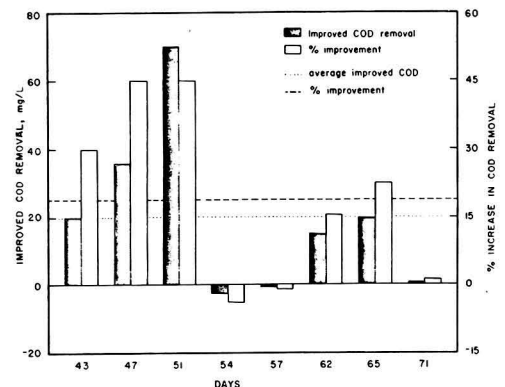
FIGURE 2. Improvement in COD removal by the PAC unit at an equilibrium PAC concentration of 160 mg/L.
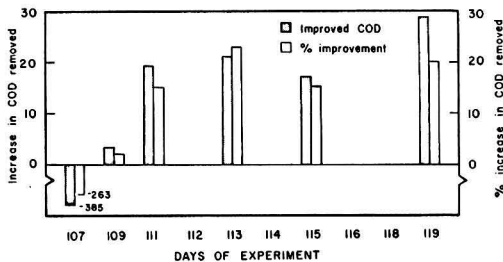
FIGURE 3. Improvement in COD removal by the PAC unit at an equilibrium PAC concentration of 20 mg/L.

various equilibrium carbon concentrations. In the figures, TOC result is presented only for the equilibrium PAC run of 280 mg/L. The test for TOC for the other PAC concentrations was discontinued; it was found in the course of the experiment that the COD and TOC of the wastewater correlate well as indicated by Figure 1.

The bar graph for the 160 mg/L PAC system indicates two times where the unit without PAC had slightly better substrate removal. However, the PAC unit removed 20 mg/L more COD on the average, which reflected an effluent concentration improvement of 20 percent. Furthermore, the 160 mg/L PAC unit showed more effluent variability than the 280 mg/L PAC unit. Calculations show that the mean inlet COD to the system during the period of 280 mg/L PAC run was 2820 mg/L with F/M ratios of 0.55 and 0.67, respectively for PAC unit and the biological control unit, whereas the COD loading during the trial run of 160 mg/L PAC was 3520 mg/L with F/M ratios of 0.69 and 0.78, respectively for PAC unit and the control unit. Clearly, the units were subjected to higher organic
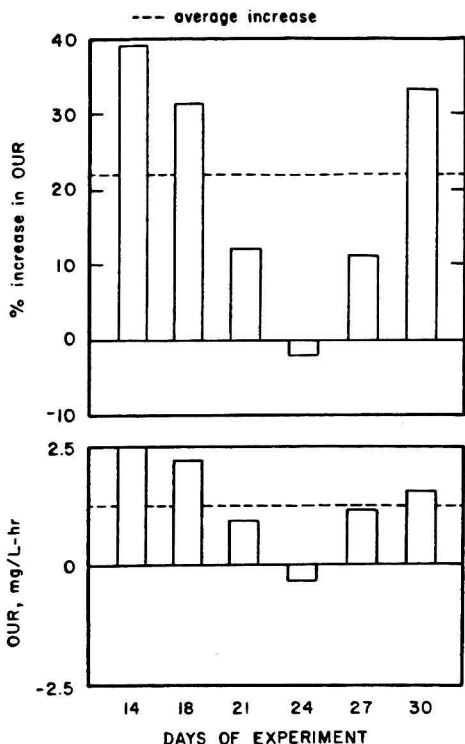
FIGURE 4. Improved oxygen uptake rate by the PAC unit at 280 mg/L PAC.
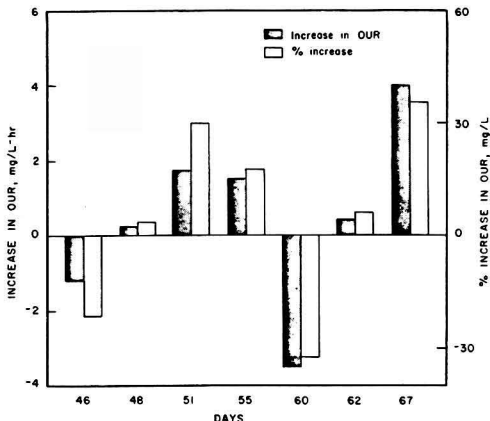
FIGURE 5. Improved oxygen uptake at PAC concentration of 160 mg/L.

loadings during the 160 mg/L PAC run. Therefore, the higher effluent COD concentrations and the considerable variability in the effluent quality could logically be ascribed to the higher F/M ratios.

Shown in Figure 3 is the graph for enhanced COD removal in mg/L and the percent improvement for the experimental run of 20 mg/L PAC. It is seen from the graph that all the data were good except one. On the day shown in the graph, the unit with PAC had a higher inlet volumetric flow rate than the bioreactor without PAC due to the malfunctioning of the pump. It was also observed that the effluent carboys had different volumes of the effluent liquid. The liquid volume of the unit with PAC was three times higher than that without PAC. That is, the PAC bioreactor unit had an organic loading within the 24-hour period that was approximately three times greater than the loading received by the bioreactor without PAC. This was reflected by low DO value taken that day. Once the problem was corrected, the PAC unit showed better COD removals throughout the period of the run. The mean COD removal in mg/L, and the average percent removal were calculated by dropping the questionable data.

Oxygen Utilization Rate (OUR)

The oxygen uptake rates in the PAC units were usually higher than the uptake rates in the control units. The mean increases in the uptake rates, and the mean percent increases for the three runs are presented in Figures 4, 5, and 6. As the bar graphs show, there were occasions when the control unit oxygen uptake rate was greater, but these were the exception. It can be seen, on the average, that the PAC units had a greater rate of oxygen consumption than the control units. The biomass concentration in the PAC units was always greater than that in the controls as indicated by the average pseudo-steady
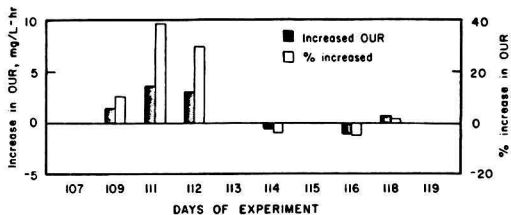
FIGURE 6. Trend of oxygen uptake rate increases for the 20 mg/L PAC unit.

Table 1 Biological Response Data from Units

Unit	MLVSS mg/L	COD Removed mg/day	Specific Substrate Utilization Rate, day^{-1}	Specific Oxygen Utilization Rate, day^{-1}
20 mg/L PAC	1220	3210	0.689	0.24
Control	1020	3190	0.819	0.28
160 mg/L PAC	1340	3450	0.674	0.16
Control	1190	3430	0.755	0.18
280 mg/L PAC	1340	2780	0.543	0.139
Control	1110	2760	0.652	0.142

state MLVSS of the bioreactors presented in Table 1. The greater biomass in the units would have been responsible for the greater oxygen utilization they exhibited.

The specific oxygen uptake rates (SPOUR) of the bioreactors revealed that the PAC oxygen utilization rates were greater only because of greater biomass. The SPOUR values for the control units were always higher than the PAC units, indicating that the control unit biomass was more active, even though it removed less substrate, and used less total oxygen. Interestingly, the increase in the SPOUR difference between units was inverse to the PAC concentration in the PAC unit. This is inverse of what it should be if the addition of PAC was responsible for the lesser SPOUR values in the PAC units. It was speculated that the SPOUR differences were because of the lesser MLVSS concentrations in the control units, which resulted in a higher F/M ratio.

Comparative Performance

The increases in COD removal were 14, 20, and 18 mg/L
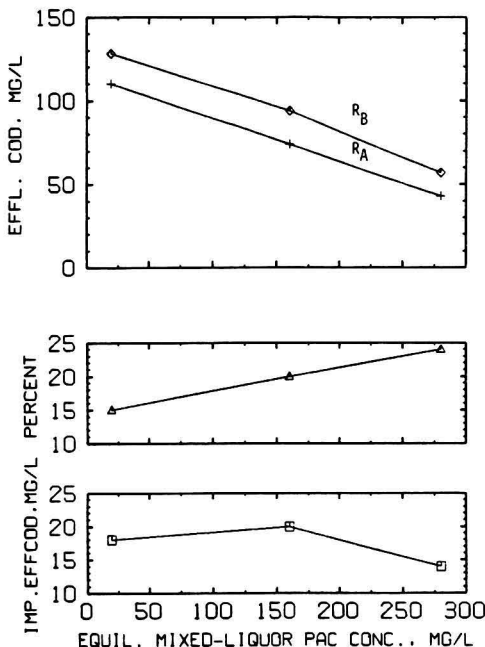
FIGURE 7. Effect of various PAC concentrations on the effluent COD at MCRT of 14 days.

at the respective equilibrium PAC concentrations of 280, 160, and 20 mg/L. Evidently the improvement in milligram per liter could not be related to the PAC concentrations. However, when expressed as percent improvement, an apparent linear relationship with PAC concentration was obtained. But extrapolation of the line to a PAC concentration of zero indicates that the PAC units were 14 percent more effective than the control units in removing COD, independent of the PAC in the units. This explanation is illustrated in Figure 7. A plausible explanation for the poor correlation between the PAC doses and the improved removals could only be ascribed to the small quantities of slowly biodegradable organics and toxic organic compounds present in the wastewater. Thus, as they were biologically sequestered at a particular carbon dose, higher carbon doses did not discernibly improve the purifying capacity of the treatment process. The result data agree well to the findings of other workers [1, 2].

It is possible that the greater biomass observed in the PAC units of this investigation was the result of the accumulation of somewhat biodegradation-resistant organics in the pores of the carbon particles, which ultimately resulted in greater colonization of the macropores, greater substrate, and therefore, larger biomass. However, if this were true, it should be possible to account for the increased biomass by the increase in COD removal. In fact, this could not be done. For instance, the increased biomass concentration in the 280 mg/L PAC unit compared to the control unit was 230 mg/L. The increased effluent COD removal, however, was only 14 mg/L. Thus, using the inlet flow rate, the volume of the reactor and the MCRT, the increased COD removal was 61 mg per day, but the biomass increase was 271 mg per day. This represents a 16 percent contribution to the increase in biomass by the increased COD removal. Clearly, the increased COD removal would not by itself account for the increase in biomass.

The method of obtaining the volatile fraction of the activated carbon might have been too conservative, and, therefore, the amount subtracted from the total MLVSS might have been too small. This would have resulted in an MLVSS concentration for the PAC units that was higher than it should have been, based on biomass only. If this were true, however, the increase in MLVSS over control should have been a function of the PAC concentration, but this was not the case. The increase in the 20 mg/L PAC units was 209 mg/L, whereas the MLVSS increase in the 160 mg/L PAC unit was only 150 mg/L. Furthermore, the increase in MLVSS in the 20 mg/L PAC unit was only a little less than the increase in the 280 mg/L PAC unit, which increased by 230 mg/L. The inconsistency between the 20 mg/L PAC unit and the two PAC units is obvious. Again, inaccurate determination of the activated carbon contribution to MLVSS is the most likely explanation for the biomass in the 160 mg/L, and 280 mg/L PAC units that could not be accounted for. The increase in the 20 mg/L PAC unit is too large for such an explanation, but the cause is unknown.

The biological response data for the experimental units shown in Table 1 indicate that the responses were consistent with a real increase in MLVSS in the PAC units. Because the MLVSS concentrations in the PAC units were larger than those in the control units, the control units had higher apparent specific substrate utilization rates than the PAC units, even though the total substrate removals in the PAC units were greater.

Plots of effluent COD and specific oxygen utilization rates with specific substrate utilization rate depicted in Figure 8 indicate that the responses of the various units were related to the specific substrate utilization in the units, regardless of the PAC concentrations, which implies that a significant fraction of the apparent MLVSS was real.

Biokinetics and the Yield

A mass balance for substrate around the bioreactors resulted in the following equation:
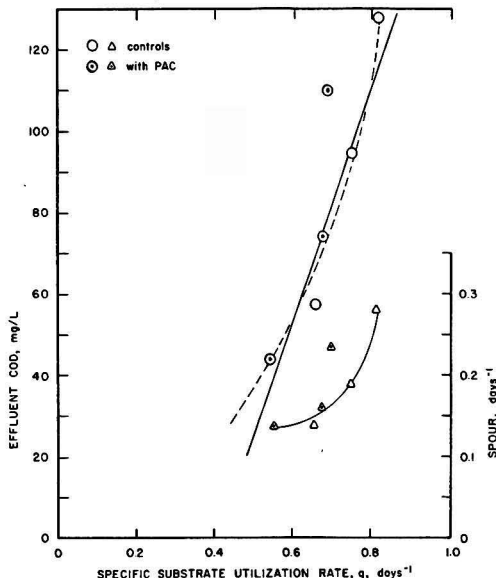
FIGURE 8. Correlation of system responses with apparent specific substrate utilization rate.

FIGURE 9. Relationship between zone settling and effluent suspended solids concentration.

$$\left(\frac{1}{X}\right)\frac{dS}{dt}=\frac{Q(S_0-Se)}{XV} \qquad (1)$$

where $(1/X)dS/dt = q$, the specific utilization constant, T^{-1}; Q = volumetric flow rate, L^3T^{-1}; X = active biomass in the aeration vessel ML^{-3}; S_0 = inlet substrate measured as COD, ML^{-3}; S_e = effluent substrate measured as COD, ML^{-3} and V = volume of the aeration vessel, L^3. In addition, the substrate removal rate, based on Monod's microbial kinetics, is represented as:

$$\frac{dS}{dt}=\frac{KXS}{K_s+S} \qquad (2)$$

The bioreactors were completely mixed in this study, and therefore, the COD in the aeration vessel was essentially equal to the effluent COD measured. Furthermore, making the assumption that the effluent COD was infinitesimal as compared to the saturation constant, K_s, then

$$\frac{dS}{dt}\bigg|X=\left(\frac{K}{K_s}\right)S_e=K_bS_e \qquad (3)$$

Where K_b is the pseudo-first order kinetic constant, $L^3M^{-1}T^{-1}$. Replacing the left hand side of Equation (1) with the right hand side of Equation (3) results in the following:

$$K_bS_e=\frac{Q(S_0-S_e)}{XV} \qquad (4)$$

Mathematically, the observed cell yield coefficient Y_{obs} is defined as:

$$Y_{obs}=\frac{\left(\frac{dX}{dt}\right)}{X}\bigg/\frac{\left(\frac{dS}{dt}\right)}{X}=\mu/q=\frac{1}{\theta_c q} \qquad (5)$$

Equations (4) and (5) were the basis of evaluation of the effects of PAC on the first-order biokinetics parameter and the stoichiometric cell yield coefficient.

Table 2 summarizes the biokinetic constants for various carbon dosages and their biological control values at a temperature of 18°C. The data show that for each run, there was an increase in the observed cell yield coefficient. However, the increase was less proportional to the increasing equilibrium PAC concentration.

The first order kinetic constant also increased with the addition of PAC except the value for carbon dose of 20 mg/L. As the table indicates, decreasing the equilibrium PAC concentration tended to decrease the first order constant, K_b. Apparently, the results of the pseudo-first order kinetic constant show that the total microbial activities with PAC units were better.

ZSV and Effluent SS

The addition of PAC to the activated sludge clearly improved the settleability of the sludge. The ZSV was higher and the

Table 2 Biokinetics Constants for Various Carbon Dosages and Their Biological Control Values at Temperature of 18°C

*Parameters	280 mg/L		160 mg/L		20 mg/L	
	R_A	R_B	R_A	R_B	R_A	R_B
Y_{obs}	0.132	0.110	0.106	0.0946	0.104	0.0872
K_b, L/mg · day	0.0126	0.0114	0.00911	0.00803	0.00626	0.00640

*Parameters are expressed in terms of COD.
R_A = PAC unit
R_B = control unit

SVI lower for each PAC unit compared to its control unit. The greater improvement occurred in the 280 mg/L unit, but it and its control also had the lowest ZSV value and the highest SVI value observed during the study. SVI improvement showed a better correlation with PAC dose than did ZSV improvement. The correlation was not linear, but SVI did improve more as the PAC concentration increased. By contrast, the 20 mg/L PAC unit had a greater improvement compared to its control than did the 160 mg/L PAC unit.

Nonetheless, this experiment indicates that PAC did not significantly reduce the effluent suspended solids of the units as would be expected with improved settleability. In spite of these results, it seems clear that PAC added considerable weight to the flocs and improved settleability. However, this apparently worsened the effluent suspended solids concentration because the smaller particles separated from the settling blanket. Thus, as shown in Figure 9, as the ZSV increased, the effluent suspended solids increased.

CONCLUSIONS

The various equilibrium PAC concentrations enhanced organic substrate removal as reflected in the higher first order kinetic constant, K_b. The observed cell yield coefficient also increased with the addition of PAC. The apparent mechanism of enhanced COD removal was the stimulation of greater biomass growth.

The effluent suspended solids concentrations from the PAC units were usually higher; the primary factor affecting the effluent SS was the zone settling velocity (ZSV) of the activated sludge. Thus, the higher the ZSV, the higher the effluent SS. This finding implies that PAC addition may not be the appropriate approach for upgrading the wastewater treatment plant to meet the future effluent guidelines.

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