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

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Cover: An Amcecc custom designed multi-adsorber system (see story on page S4). Photo courtesy of Amcecc Adsorption Systems, Schamburg, Illinois.

ENVIRONMENTAL PROGRESS

DEPARTMENTS

Editorial.....	S2
Environmental Update.....	S3
Book Reviews.....	S7
Software Review.....	S11
Environmental Cost Indexes.....	S15

REMEDIATION

The Haztimator Knowledge-Based (Expert) System: Providing Design and Time/Cost Estimates for Hazardous Waste Remediation <i>Jeff Staudinger, Gaye A. Oralkan, Raymond E. Levitt and Paul V. Roberts</i>	82
Pb Mobility and Extractant Optimization for Contaminated Soils <i>I.A. Legiec</i>	88

AIR

Simultaneous Hot Desulfurization and Improved Filtration in Coal Utilization Processes <i>Gina Kennedy, Paul Eggerstedt, James F. Zievers and Elizabeth C. Zievers</i>	93
Parametric Testing of Coal Electrostatic Precipitator Performance <i>L. Cañadas, B. Navarrete, P. Ollero and L. Salvador</i>	98
Hindcasting Volatile Chemical Emissions to Air from Poned Recycle Oil <i>Louis J. Thibodeaux and James C. Carver</i>	106
Industrial Boiler Retrofit for NOx Control: Combined Selective Noncatalytic Reduction and Selective Catalytic Reduction <i>Paul W. Groff and Brian K. Gullett</i>	116

WATER

Whole Effluent Toxicity Reduction by Ozone <i>Brandon R. Ball, K.V. Brix, M.S. Brancato, M.P. Allison and S.M. Vail</i>	121
Photocatalyzed Oxidation of Phenol in Water Using a Cocurrent Downflow Contactor Reactor (CDCR) <i>J.M. Winterbottom, Z. Khan, A.P. Boyes and S. Raymabasay</i>	125
New Techniques for Solvent Recovery and Elimination of Wastewater Emissions during Vacuum Process Operations <i>Barry A. Perlmutter</i>	132
Reductive Dehalogenation of Trichloroethylene Using Zero-Valent Iron <i>J. Gotpagar, E. Grulke, T. Tsang and D. Bhattacharyya</i>	137

WORLDWIDE DISTRIBUTION
1997

Water Supply Challenges in the 21st Century

E. Timothy Oppelt

National Risk Management Research Laboratory, Cincinnati, OH 45268

Until recently, most of the emphasis of our National drinking water regulations and standards has been on assuring the effectiveness of water treatment. The fate of drinking water, once it leaves the treatment plant and travels to the point of consumption has received less attention. There is substantial evidence, however, that many factors can cause the quality of water to deteriorate after treatment. Microbial pathogens, for instance, can be introduced to distribution systems in many ways including; piping failures, construction activities, back pressure, sewage cross-connections and poor system design and operation practices which can promote stagnant zones with low disinfectant residual. In addition to microbial contamination, chemical degradation of water quality may also occur in distribution systems. In some systems, lead and copper can be leached from distribution piping and household plumbing at concentrations of concern for public health. Potential carcinogenic organic compounds formed as by-products of water disinfection may also degrade drinking water quality. While these are initially formed during treatment, it is well established that levels increase with time in the distribution system with as much as 50% of the total by-product formation occurring there.

The American Water Works Association Research Foundation has estimated that there is 880,000 miles of underground distribution piping in the U.S. with a replacement value of \$348 billion. Much of this has been installed since World War II and is believed to be in good condition. However, about 27% is unlined cast iron and steel pipe that is judged to be in only fair or poor condition. Older utilities have a predominance of aging infrastructure in poor

condition which will require accelerated repair or replacement. Unfortunately, even at the current annual U.S. rate of water system capital investment of \$3.3 billion, most utilities will be able to replace a given pipe only once every 200 years. In fact, the U.S. EPA in its January, 1997 Drinking Water Infrastructure Needs Survey, estimated U.S. drinking water will need to spend \$138.4 billion in infrastructure over the next 20 years in order to meet the requirements of the Safe Drinking Water Act. The Survey projected that 56% of this amount would be needed for transmission and distribution system installation and replacement.

These deficiencies in the structural integrity of drinking water distribution systems, as well as the effectiveness of current design and operational practices, can have real health consequences. Since 1993, for instance, nearly 850 community water systems have been ordered to issue public boil water advisories due to bacterial contamination from all causes. This included highly publicized distribution system problems in a number of large cities such as New York and Washington, D.C. Distribution system failures in two small Missouri cities, Cabool and Gideon, are believed to be linked to hundreds of cases of intestinal illness and 11 deaths there.

As we move into the twenty-first century, water treatment and distribution systems will face many challenges as they work to meet increasingly stringent treatment standards and assure adequate quantity and quality of source water for growing customer demand. If water quality at the point of use is also to be preserved, however, greater attention will need to be given to the design, operation, and maintenance of distribution systems. Communities that have often taken continued urban infrastruc-

ture integrity for granted will need to make prudent improvement investments, aided by resources that will become available for water infrastructure development from the Federally-supported State Revolving Funds. Engineers must focus greater attention on designing distribution systems to ensure water quality as well as hydraulic reliability. This could include installation of sensors for real-time monitoring of important distribution system quality indicators such as disinfectant residual, water pressure, flow direction, microbial densities, total organic halides, and others. These innovations, in combination with improved designs and geographic information based systems for modeling water quality and flow offer the potential for more rigorous operation and management of distribution systems in the future.

For its part, the U.S. EPA is beginning to focus a greater degree of its research resources on the problems of distribution systems. This includes continuing improvement of the capability to model and predict water quality in distribution systems, understanding the role of biofilms in the microbial safety of water, improved storage tank designs that promote mixing and avoid zones of low disinfectant residual and improved technology to manage corrosion by-product and disinfection by-product formation in distribution systems.

The U.S. has one of the best water supply systems in the world. If we are to preserve this, and in fact improve it, a significant investment in resources, engineering innovation and research related to distribution infrastructure will be required from communities, water utilities, design firms and state and Federal water authorities into the twenty-first century.

E. Timothy Oppelt, Director of the National Risk Management Research Laboratory, has been with the U. S. Environmental Protection Agency since 1970. He has a B.S. in Civil Engineering, an M.S. in Sanitary Engineering, and an MBA degree.

Mr. Oppelt can be reached at the U.S. EPA/NRMRL (Ms-235), 26 Martin Luther King Drive, Cincinnati, OH 45268.

NEW HANDBOOK DEALS WITH PROCESS INDUSTRY WASTE MANAGEMENT

The British-based Institution of Chemical Engineers (IChemE) recently released *Management of Process Industry Waste: An Introduction*. The book, written for new engineers and others requiring a rapid overview, addresses every facet of waste management, including laws and regulations, process and waste characterization, waste minimization, on-site waste treatment, off-site waste disposal plus health and safety issues.

Chapters address topics such as monitoring, developing and using waste databases, reviews and audits, selection of treatment methods, transport of waste, and special safety and health issues, such as handling volatile organic compounds, biological hazards, corrosivity, and use of anaerobic digesters.

Even though most of the regulatory information and references are British, the technology presented is universal. In fact, the book's unique European perspective makes it an invaluable resource for companies currently working there, or contemplating entering that market.

Management of Process Industry Waste: An Introduction [ISBN 0-85295-324-0] consists of 172 pages, hardcover. The U.S. list price is \$65. To order a copy please contact the AIChE Express Service Center at 1-800-AIChemE (1-800-242-4363); fax: (212)705-8400; e-mail: xpress@aiche.org.

COURSES ON SITE CHARACTERIZATION AND REMEDIATION OFFERED BY AIChE

AIChE is offering a new two-part course on Site Characterization and Remediation to take place in Denver in June and Philadelphia in September.

Part I entitled Site Characterization Including Feasibility Studies focuses on strategies and methods to acquire the necessary data to develop solutions to contamination problems. The emphasis is on how to streamline and maximize the benefit of data collection activities, while simultaneously minimizing cost. Site investigation techniques covered include: historical research, preparation of data quality objectives, contaminant transport, sampling and quality assurance plan preparation, field screening, vadose zone sampling, soil sampling, container sampling, groundwater sampling, introduction to risk assessment, conceptual model

development, development of remedial action objectives, and feasibility studies. Part I of the course will take place in Denver, June 3 through 5 and Philadelphia September 8, through 10. The fee is \$1,145 to AIChE members; \$1,245 for others.

Part II of the course is entitled Groundwater and Soil Remediation: Remediation Techniques, Systems Design, and Cost Estimating for Cleanup. The course focuses on understanding remediation options; designing remediation systems; estimating costs where metals, hydrocarbons, and chlorinated solvents are contaminants of concern. The techniques explained can be used in manufacturing industries, defense installations, governmental and municipal institutions, and gasoline stations. Emphasis is mainly on proven techniques rather than on methods which have not yet been commercially developed and used on a wide scale. Upon completion participants should be able to use the results of remedial investigations to organize feasibility studies, remediation systems design, and cost estimates for installing and operating remediation equipment. Part II of the course will take place in Denver June 6-7, and Philadelphia, September 11-12. The fee is \$845 for AIChE members and \$945 for others.

For more information, or to register, please contact the AIChE Express Service Center at 1-800-AIChemE (1-800-242-4363); fax: (212) 705-8400; e-mail xpress@aiche.org.

GREAT LAKES TO BE FREE OF TOXIC SUBSTANCES BY 2006

Last month, EPA administrator Carol Browner and Canadian Minister of the Environment Sergio Marchi signed an agreement to virtually eliminate persistent toxic substances from the Great Lakes by the year 2006. The agreement was signed during Prime Minister Cretien's first official visit to Washington as Canadian prime Minister.

This is the first time specific reduction targets for toxic pollutants have been jointly set by both countries, although it is on a voluntary compliance basis. Browner and Marchi signed additional agreements to expand efforts to control transboundary air emissions and to cooperate in a number of environmental research and development activities.

The Great Lakes are polluted from the air, stirred-up bottom sediments, urban

and agricultural runoff, hazardous waste sites, plus industrial and municipal wastewater. All the Great Lakes states have fish consumption advisories based primarily on PCB, mercury and toxaphene contamination.

According to the Environmental News Service the agreement calls for the U.S. to implement a 50% reduction of mercury uses nationally; a 90% reduction nationally of PCBs used in electrical equipment; a 75% reduction in total releases of dioxans and furans from human activity sources, such as incinerators, to apply to aggregate releases to the air nationwide and of releases to the waters of the Great Lakes; and confirmation that there are no releases of five bioaccumulative pesticides: chlordane, aldrin/dieldrin, DDT, mirex and toxaphane.

EPA, Environment Canada, plus industry, labor, states, provincial, local and tribal governments will implement the strategy. The plan is based primarily on voluntary activities but builds on existing U.S. and Canadian regulatory programs.

HENRY K. SHAW RECEIVES THE 1997 LARRY K. CECIL AWARD

Henry K. Shaw was presented with the AIChE Environmental Division's 1997 Larry K. Cecil award at AIChE's Spring National Meeting in Houston. The award recognizes outstanding chemical engineering contributions and achievement in the preservation or improvement of the environment.

An AIChE Fellow, Shaw has been active in AIChE's Environmental Division since its founding in 1970. He currently serves as the division's vice chair, and he is also a member of the editorial board of *Environmental Progress*.

The author of 55 publications and 3 patents, Shaw was an AT&T Industrial Ecology Faculty Fellow from 1994 to 1996. He chaired the Chemical Technology Division Advisory Committee to the Director of the Oak Ridge National laboratory and the Engineering Foundation Board, and was an invited participant for the U.S. Senate's National Commission on Air Quality and in several national Research Council studies.

His current research includes pollution prevention by solvent substitution, thermal destruction of hazardous wastes using conventional and catalytic incineration, scrubbing of acid rain precursors, packed and fluidized bed adsorption of acidic flue

gas components, and control of soot/NO_x in diesel engines.

Shaw joined the faculty of New Jersey Institute of Technology (NJIT) in 1986 after 28 years of industrial experience with Exxon Research and Engineering, Mobil Oil, and Babcock & Wilcox. He earned his BChE from the City College of New York, an MS in chemical engineering from NJIT, and a PhD in physical chemistry and MBA from Rutgers University.

LEDERMAN CHAIRS GOVERNMENT RELATIONS COMMITTEE

Peter B. Lederman recently assumed the chair of the AIChE Government Relations Committee (GRC). Lederman is a past chair of the AIChE Environmental Division and has contributed many interesting articles to *Environmental Progress*. He is Director of the Center for Environmental Engineering and Sciences at the New Jersey Institute of Technology.

The GRC leads AIChE's programs for interaction with government, which seek to enhance AIChE's reputation among government officials and the public as a credible source of assistance and information on policy issues that impact chemical engineers.

CCPS OFFERS RMP AND PSM COMPLIANCE COURSES

AIChE's Center for Chemical Process Safety (CCPS) has developed courses for those involved in helping their organizations comply with EPA's RMP (Risk Management Plan) and OSHA's PSM (Process Safety Management) standards.

A three-day course entitled "Process Safety Management Systems" is designed to provide PSM principles for developing and implementing programs to comply with OSHA (Occupational Safety and Health Administration) PSM standard 1910.119 and EPA (Environmental Protection Agency) RMPs. Attendees will learn how to develop, maintain, and evaluate the success of a PSM program. In addition to course notes, attendees will receive the CCPS book entitled *Guidelines for Technical Management of Chemical Process Safety*. The course will take place June 23-25, in San Diego and September 15-17, in Houston. Registration is \$1,145 for AIChE members and \$1,245 for others.

The next step is covered in the course entitled "Documenting and Auditing Process Safety Management." This two-day course provides guidance and materials to those responsible for auditing the elements of PSM, as required by OSHA's PSM standards and EPA's RMP rules.

Attendees will acquire knowledge of the types and quantities of information generated when implementing a PSM program. They will learn how the flow of information links PSM elements and documentation practices to ensure that PSM information is effectively communicated to users.

In addition to course notes, attendees will receive the CCPS books *Guidelines for Auditing Process Safety Management Systems* and *Guidelines for Process Safety Management Documentation*. The course will be offered September 18-19 in Houston. The registration fee is \$845 for AIChE members and \$945 for others.

For more information, or to register please contact the AIChE Express Service Center at 1-800-AIChemE (1-800-242-4363); fax: (212) 705-8400; e-mail express@aiche.org.

UPCOMING EPA REMEDIATION MARKET CONFERENCES

EPA has scheduled this year's remediation market conferences. The Midwest conference will take place July 22-23 in Chicago. The South Central United States conference is slated for New Orleans in November.

According to EPA's *Tech Trends* the conferences provide a forum for federal, state, and private organizations to describe

Tough process problem? Practical Engineering Perspectives Has the Plant-Proven Answers

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Introduction by Stanley S. Grossel

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opportunities to participate in various clean-up programs and provide information on assistance programs and resources available to developers.

For further information please contact Naomie Smith (703) 603-7186 or Ann Eleanor (703) 603-7199.

U.S. ENVIRONMENTAL MARKETS REPORT FOR 1997-2000 AVAILABLE

Richard K. Miller & Associates have released the eighth edition of their annual environmental markets report. *U.S. Environmental Markets: 1997-2000* includes assessments of current U.S. pollution control and waste management expenditures, discussions of trends, and forecasts. In addition to an in-depth analysis of each market sector, the report provides insight into many emerging market opportunities.

Incidentally, *U.S. Environmental Markets: 1997-2000* presents an optimistic market outlook. According to the report environmental firms have adjusted to declining regulation-based market drivers, and new directions. New short-term opportunities have emerged to compensate for declining market sectors.

The cost of the study is \$485. For more information please contact Richard J. Miller & Associates Inc., 5880 Live Oak parkway, Suite 270, Norcross, GA 30093. Telephone (770) 416-0006.

FREE EPA ENFORCEMENT SEMINAR

The combined level of EPA criminal, civil and administrative fines and penalties in 1996 totaled \$173 million, the highest in EPA history, according to the Environmental Resource Center. The center is offering training for those wishing to avoid being part of this year's statistics.

Training is offered on EPA, OSHA, and DOT regulations including hazardous waste management, hazardous materials management, OSHA Haz Com, storm water permitting, the Clean Air Act, plus environmental property transfers.

For training through August, one person in a team of three sent to the same training seminar can attend the seminar for free. For more information see Environmental Resource Center home page at <http://www.ercweb.com>, or call 1-800-537-2372.

For a schedule of upcoming courses please fax a request to (919) 469-4137 or e-mail to: kgarde@ercweb.com. Requests by mail should be sent to the following address: Buy 2, Get 1 Free Training Offer, Environmental Resource Center, 101 Center Pointe Drive, Cary, NC 27513.

SYSTEM SOLVES VOC PROBLEMS WHILE RECOVERING SOLVENTS

Tougher emissions requirements by the Bay Area Quality Management District mandated the San Jose facility of Quebecor printing to look for other options to control their proof press exhaust. Space constraints and earthquake zone construction requirements made enlargement an expensive proposition. Furthermore the proof press was at the opposite end of the gravure press hall from the existing solvent recovery system and the long main solvent-laden air suction duct was at the limit of its capacity and would require upgrading to handle the extra air flow.

The Hybrid Concentrator, from Amccc Adsorption Systems, located in Schamburg, Illinois, was selected to control the proof press exhaust (see photo on the cover of this issue). Hybrid concentrators are specifically designed to capture low concentrations of VOCs from large air volumes. A slowly rotating adsorption wheel is used for truly continuous operation. Most of the wheel is capturing the VOCs while a small segment is regenerated by a small flow of hot air.

Typically, a 95 percent adsorption performance is attained. The VOC-concentrated air flow (1500 cfm) is then sent to the suction duct of the main solvent recovery system where the deep bed carbon adsorbers capture the solvent for reuse.

Because the regeneration air from the concentrator to the main recovery system was only a 1 percent increment to the main system's capacity, the volume could be processed without modification to the main system.

Filters capture any ink and paper particulate. The solvent-laden air is also cooled since the lower the temperature the better the performance of activated carbon.

A sacrificial bed of activated carbon protects the honeycomb adsorption wheel from any high boiling point organics that may have evaporated from the inks.

The concentrator was designed for 18,000 cfm. It was factory assembled, transported to the job site, and installed adjacent to the proof press room. The unit required electricity, cooling water for the coils, and steam for the regeneration heater - all were available nearby.

Operating requirements are low: 50 kW for fan motors and 300 pounds /hour of steam for the regeneration heater.

The concentrator solved a potentially expensive VOC control problem. It avoided expansion of the main recovery system and a major new suction duct. The installed cost for the project was about \$25 per cfm. For more information please contact Mike Worrall at (847) 706-6365. Fax: (847) 706-6370.

The PEP Book Series

New from AIChE Publications

The PEP series compiles the most useful articles from recent AIChE publications into fully indexed, single-topic references. Designed for on-the-job use, each volume features a wealth of practical, "how-to" information, written by working engineers and packed with "hands-on" strategies you can apply directly to your own plant operations.

Plant Safety

Foreword by Stanley S. Grossel
Published September 1996 272 pages
Pub Q-1 ISBN 0-8169-0709-9

When it comes to safety in the CPI, up-to-date information isn't just an advantage, it's an absolute requirement. That's why this new collection is an essential industry sourcebook, containing practical, "how-to" reports by top experts on everything from explosion quenching speeds, to designing a complete plant safety program. Several of the articles are the result of major industry-wide research efforts launched by AIChE. Many relate directly to the OSHA Process Safety Law of 1992, and to the new EPA Risk Management Program passed earlier this year.

Coming soon from PEP:

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Introduction by Alan P. Rossiter
Pub Q-3 • ISBN 0-8169-0711-0

The Environment: Air, Water and Soil

Introduction by Alan P. Rossiter
Pub Q-5 • ISBN 0-8169-0713-7

Edited by Gail F. Nalvin and the editorial staff of AIChE, all PEP volumes are hardcover and sell for \$85 per copy in North America and \$120 elsewhere.

AIChE members pay \$68 per copy (North America), \$96 (International). To order, please call 1-800-242-4363. Outside the US and Canada please call (212) 705-8100.

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MICROBIAL TRANSFORMATION AND DEGRADATION OF TOXIC ORGANIC CHEMICALS

Lily Y. Young and Carl E. Cerniglia, Wiley-Liss Inc., New York, NY, (1995), 654 pages, [ISBN No.: 0-471-52109-4], U.S. List Price: \$99.95.

The knowledge that microorganisms are capable of degrading toxic organic chemicals is not a recent discovery. What is new is our understanding of the basic pathways and mechanisms of microbially mediated biodegradation and the successful demonstration of toxic chemical biodegradation both in the laboratory and in the field. This book draws together information about the different kinds of toxic chemicals, microorganisms, enzymatic pathways, genetics, laboratory reactor designs and field applications. It presents the current state-of-the-art in toxic chemical biodegradation.

The book is organized into four parts. Part 1 examines the diversity and versatility of the microorganisms involved in the degradation of hazardous chemicals and the sources and types of chemicals that are found in the environment. Part 2 explores the enzymes and pathways for biodegradation of the major classes of toxic chemicals. Part 3 covers the application of the technology in the field for the biotreatment of toxic chemicals such as solvents, chlorinated aromatics and petroleum wastes. Part 4 looks to the future and covers the use of molecular biology to develop new approaches to study and improve biodegradation technology.

Consisting of seventeen chapters, the book contains a great amount of detail. The authors have provided comprehensive coverage of each research topic. Each chapter has an extensive list of references that makes this book a good reference text. Only one chapter on risk assessment for toxic chemicals did not appear to be relevant. A few of the many topics covered are: petroleum hydrocarbon metabolism, treatment of coal tar-contaminated soils, bioremediation of BTEX, reductive dechlorination of polychlorinated biphenyls, bioremediation of chlorophenol wastes, mechanisms of polycyclic aromatic hydrocarbon degradation, and organopollutant degradation by lignolytic fungi.

In summary, the book is recommended as a reference text that summarizes the state-of-the-art in toxic organic chemical metabolism and remediation. It covers both the theory that has been discovered in the

laboratory and the application of this knowledge in the field. It should appeal to both academic researchers and environmental engineers.

Edward J. St. Martin, Ph.D.
Research Area Leader, Bioprocessing
Energy Systems Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

HANDBOOK OF POLLUTION AND HAZARDOUS MATERIALS COMPLIANCE

Nicholas P. Cheremisinoff and Madelyn Graffia, Marcel Dekker, Inc., New York, NY, (1996), 506 Pages, [ISBN No.: 0-8247-9704-3], U.S. List Price: \$185.00

This book is intended as a guide and a working reference to assist environmental and health and safety managers in complying with the ever-growing code of environmental regulations. The authors also state that the book was written as a textbook for environmental management students. In many ways the book satisfies these objectives for the intended audience and also includes information that would be useful to risk managers in the private sector. The book also has a message for those representatives of the business community that may not yet understand that failure to comply with environmental regulations can negatively impact the bottom line and preclude, or at least complicate the sale or transfer of assets.

Unfortunately, the authors begin the book rather abruptly, missing the opportunity to highlight the "motifs" common to the environmental regulatory programs detailed in each chapter such as: the fact that many environmental statutes were crafted in response to environmental disasters, for example: Love Canal, N.Y. (Comprehensive Environmental Response, Compensation, and Liabilities Act [CERCLA]), Bhopal, India (Superfund Amendments and Reauthorization Act [SARA Title III]) and the detection of trihalomethanes in New Orleans, LA. drinking water (Safe Drinking Water Act [SDWA]). Other common themes not discussed globally by the authors include the fact that the same substances or classes of substances are regulated in several regulatory programs and the fact that the concept of "best technology" is relied upon for pollution control and/or treatment in several programs. In a similar fashion, the book ends without a summa-

tion chapter emphasizing these overarching themes.

Despite these imperfections, the book should serve environmental and safety managers well as a source book for information about the byzantine environmental regulations in effect today. The book provides an excellent overview of the alphabet soup of environmental and safety statutes/regulations that impact, or that could impact, the public and private sectors including: Occupational Safety and Health Act (OSHA), Clean Air Act (CAA), Clean Water Act (CWA), SDWA, CERCLA, SARA, Resource Conservation and Recovery Act (RCRA), Toxic Substances Control Act (TSCA), National Emission Standards for Hazardous Air Pollutants (NESHAPS), and the Federal insecticide, Fungicide, and Rodenticide Act (FIFRA).

In general, the book devotes a chapter to each of the primary regulatory programs and offers an introduction to the applicable statute/regulations, a historical perspective, a discussion on the applicability and intent of the program, and a description of how the program functions to satisfy the statutory intent. In many chapters the authors have included useful tabular summaries of such key points as a listing of priority pollutants, a summary of Federal environmental statutes impacting water utilities, EPA drinking water standards, and a summary of major Federal environmental statutes. In many cases, chapters also include a description of the industries effected by the regulatory program, case studies, and the potential impact of future statutory changes on the regulatory program. Where applicable, each chapter discusses enforcement provisions of the regulatory program. For example, in the chapter on the CWA, there is a thorough discussion of the tools of the CWA enforcement program including: criminal penalties, civil enforcement options, citizens suits, and EPA's compliance strategy.

I personally enjoyed the historical perspective that the authors discuss for each of the major environmental programs. For example, in the chapter on the SDWA the authors discuss the fact that one the first set of drinking water standards was referred to as "Treasury Standards" because the standards were developed in 1914 by the United States Public Health Service which, at the time, was part of the U.S. Treasury Department. The authors state that the Treasury Standards applied to water supplies in interstate shipping and that the standards were developed as part of a U.S. Public Health Service (USPHS)-adminis-

tered health care program for sailors in the Merchant Marine. In the discussion on historical perspectives of the CAA the authors reference smoke control ordinances promulgated by the cities of Chicago and Cincinnati in 1881. Also of interest is the discussion of the "pedigree" of the Clean Water Act which includes the 1899 Refuse Act and the 1976 consent decree, called the Flannery Decree which the authors consider to be the heart of the CWA program as it exists today.

One of the most important chapters in the book is the chapter on managing facilities and facility transfers. The chapter discusses Federal and a number of state regulatory programs governing the transfer of potentially contaminated property. The chapter emphasizes the importance of managing operations properly, that is - in compliance with the environmental programs described in the book - in order to minimize liability. The environmental compliance audit is discussed as a tool to help site managers gauge operations. The authors also include a valuable discussion on the form and content of property transfer audits and how such audits can help both buyers and sellers manage risks associated with property transfers.

In summary, despite numerous misspellings in the text, repetitive portions of the book plus a number of inaccuracies concerning the RCRA Corrective Action program, this book is recommended as a guide for environmental and health and safety managers. The book is also recommended as an environmental program "primer" for more senior managers who want to gain an understanding of how environmental regulations can impact the profitability and liability of a business.

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BIOHAZARDS MANAGEMENT HANDBOOK

Daniel F. Liberman, editor, Marcel Dekker, Inc., New York, NY, (1995), 461 pages, [ISBN No.: 0-8247-8995-4], U.S. List Price: \$175.00

The principles involved in the management of biohazards in the laboratory are discussed in this book. It is organized into eighteen chapters grouped in three sections: (1) Facility Considerations, (2) Biosafety Principles and Practices, and (3) Regulatory Agency Considerations. This

book is a useful reference for anyone who needs to learn about or manage biohazards in a research laboratory setting. Included in this book are step-by-step procedures for implementing biohazards management programs and outlines for documenting the programs as required by regulatory agencies. A large portion of this book can be applied to any research laboratory dealing with any hazardous substance whether biological or chemical. The information is current and relevant references are provided at the end of each chapter.

A well-designed laboratory can eliminate many safety hazards, hence the purpose of the first section of the book. While much of this book is about biohazards and their management, this section can apply to anyone designing a research laboratory. The first chapter contains the process of design and construction from the hiring of an architect to construction and cost estimates. The second and third chapters are devoted to ventilation and laboratory hoods. Included in these two chapters are the basic principles of designing a ventilation system and what needs to be considered in selecting the right type of hood and air cleaning technology. Chapters 4, 5, and 6 describe the hazards associated with pest control and animal facilities and give examples of how they may be minimized by proper facilities planning, such as separation of animal activity areas from areas of human occupancy, and storage strategies for hazardous chemicals. Also included in these chapters are specific examples of methods and procedures by which these hazards can be controlled.

Chapters 7 through 15 are concerned with biosafety principles and practices. Chapter 7 reviews laboratory-acquired illness, and biosafety control measures. It briefly discusses personnel education and training. Chapter 8 is presented in three parts. Potential hazards in the biomedical laboratory are reviewed, such as biological agents, chemicals, radioisotopes, product-related hazards, animal handling, and physical stresses. Conditions which might increase the risk of adverse health outcome are discussed, such as allergies, infertility, and pregnancies. The last part outlines the content of a medical surveillance program. Chapter 9 discusses biosafety in operations dealing with biotechnology on a larger scale than what would be found in a research laboratory. This chapter starts with a discussion on the administrative mechanism for biohazard control. Specific responsibilities of corporate management, immediate and first-line supervisor, safety personnel, and employees are delineated.

This chapter also addresses controlling biohazards in the industrial setting, risk assessment, physical containment at the large scale, and process validation. The chapter ends with a short discussion on biosafety audits and a procedural outline on conducting an audit. Personal hygiene and protection are covered in Chapter 10. Topics discussed include risk assessment, responsibilities of management and employees, personal protective equipment, and personal protection practices. Chapter 11 discusses the destruction of microorganisms. Topics covered in this chapter include sterilization by heat, liquid chemical disinfectants, and the action of specific disinfectants, such as halogens, phenolic compounds, ammonium compounds, aldehydes, alcohols, and other compounds. Disinfectants used and protocols against microorganisms, such as Human Immunodeficiency Virus, Legionella pneumonia, Hepatitis B, and slow viruses are also discussed. The chapter ends with a discussion of procedures for the decontamination of various surfaces. Chapter 12 addresses types of infectious wastes, generators of biomedical/infectious waste, elements of waste management, and relevant regulations. Chapters 13, 14, and 15 discuss safety programs for the use of chemotherapy agents, the control of infections, and risks from chemicals associated with biohazard management, respectively.

The last section comprises the last three chapters, which deal with the impact of government regulations. Chapter 16 describes what the Occupation Health and Safety Act (OSHA) Laboratory Standard means, the intention of the law, relationship to other regulations, who qualifies as a laboratory, and how to administer the law. At the end of this chapter are appendices consisting of examples of Standard Operating Procedures and Chemical Hygiene Plans. Chapter 17 discusses the major components of the Hazardous Communication Standard, research laboratory exemption, and some commonly asked questions and misconceptions of the Standard. The last chapter in the book discusses implementation of a safety program for the OSHA Bloodborne Pathogen Standard. Included in this chapter are instructions on how to assemble a program plus an example of an outline for training personnel on the hazards of bloodborne pathogens.

This book provides an excellent summary of biohazards in the laboratory and biohazard management. The book is written in a way that each chapter is complete, however, there is some repetitive information. This book is an excellent reference

book and starting point for any scientist or engineer who works in a research laboratory or who administers research laboratories. It contains a lot of useful information about safety in the laboratory.

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WASTE AGE/RECYCLING TIMES' RECYCLING HANDBOOK

John T. Aquino, editor, CRC Press, Inc., Boca Raton, FL, (1995), 281 Pages, [ISBN No.: 1-56670-068-X], U.S. List Price: \$55.00

Confronted with landfill closings and the increasing cost of waste disposal waste recycling has become an important issue in the management of wastes. Ultimately recycling programs seek to recover materials which would otherwise end up in landfills and at the same time reduce the amount of waste being generated. Source reduction and recycling are expected to play increasing roles in municipal waste management strategies.

This handbook, consisting of nine chapters, is a compilation of *Waste Age/Recycling Times* articles. The articles contain general and specific information which should be of interest to solid waste professionals. The book would also be useful to and easily understand by the general public.

Chapter One of is a compendium of solid waste profiles. The chapter is divided into major categories and subcategories. The categories address specific solid wastes (glass, newspaper, aluminum, plastics, etc.). The subcategories provide information on the specific waste: physical characteristics (weight, volume, density), recycling information (recycling rates, recycled content, recycle value, amounts available for recycling), waste management practices (source reduction, recycling, composting, incineration, and landfilling), past and present recycling practices, markets, barriers and limitations to recycling, and a list of sources for additional information. The last section of the chapter discusses what should not be included with recyclables due to the deleterious effect on the recycling process.

Chapter Two is a review of how the states approach recycling, and how recycling rates are determined (included is a table with the various waste streams counted in the recycling rates). Also discussed is what the states are legislating to develop markets, and promote the use of post consumer materials.

Chapter Three evaluates the real cost of recycling (the cost of collecting and the cost of processing recyclables). This chapter provides an excellent overview of the factors affecting the recycling process.

Chapter Four takes a look at the ups and downs of the recycling markets. Some of the past factors which have affected the markets are discussed. Ways for municipalities and recyclers to share the risks of a volatile recyclables market are presented, be it privately owned material recovery facility (MRF), revenue sharing MRF, or an indexed tipping fee. The ramifications of the various approaches are discussed with examples of some of the most successful large programs in the country (Philadelphia and New York City).

The methods of collecting recyclables (segregated, blue bag, or co-mingled), the equipment used to haul the materials to be recycled (co-collection or specialized vehicles), and the pros and cons of each are reviewed in Chapter Five. Co-collection appears to be most effective (equipment, time, and cost wise) in rural settings. Examples of the successes and disappointments of the blue bag concept are detailed (New York City, Pittsburgh, Omaha, Houston, Mobile, and Chicago). Also a discussion of curbside collection of plastics and mixed paper (office and residential) is presented at the end of the chapter.

Safety issues associated with the waste processing industry are reviewed in Chapter Six. Table 6.1 is a listing of waste collection and processing industrial safety standards. This table is a good reference for the applicable regulations and where to find them. Also, Table 6.2 lists the applicable OSHA regulations. This chapter could be generalized to most industries with safety requirements.

Chapter Seven evaluates how recycling fits into the overall solid waste management strategy. Financing options (public-private partnerships, private activity bonds, tax exempt financing, and tax limitations) are discussed. The incorporation of a waste to energy (WTE) facility into an MRF is discussed as not a mutually exclusive option. If it makes economic sense, it should be evaluated as a viable option within a waste management plan. Packaging of consumer products is also discussed as a target for

source reduction. Examples of companies and products which have successfully implemented less packaging or packaging materials are presented. The last section of the chapter addresses the nuisance of curbside recycling scavengers and what options are available to mitigate the effects on recycling.

A review of how the European markets and legislation have impacted the U.S. recycling efforts, specifically, the "Greed Dot" system of Germany and the Canadian Industry Packaging Stewardship Initiative (CIPSI) is given in Chapter Eight.

The final chapter presents case studies of MRF's in Brookhaven, New York; Dallas, Texas; and Tampa, Florida.

In summary, the handbook has a wide variety of information on the recycling industry. The book is a good starting point in understanding issues about and affecting solid waste management.

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SAFETY MANAGEMENT PRACTICES FOR HAZARDOUS MATERIALS

Nicholas P. Cheremisinoff and Madelyn Graffia, Marcel Dekker, Inc., New York, NY, (1996), 350 Pages, [ISBN No.: 0-8247-9687-X], U.S. List Price: \$135.00

This 350 page text was written in response to the Occupational Health and Safety Act (OSHA) "Right to Know" or "Hazard Communication" requirements to provide understanding to professionals who may need response to a hazardous waste incident or support of operations handling hazardous materials. As with HAZWOPR training courses, this text provides a basis for compliance, but is not a stand alone replacement for basic, advanced or refresher, training of employees. Nonetheless, the eleven clearly written chapters provide an excellent reference for professionals in training and compliance in industry. Abbreviations commonly used in safety are first listed, a benefit to the novice reader.

An overview of regulations and need for hazardous waste management is given in Chapter One. An excellent table of Acts is included and main points in the chapter are underlined. Chapter two is also an

overview, of hazardous material chemistry, including a very good discussion on flammability and reactive chemicals. Redox chemistry, compatibility of chemicals, and poisons are also discussed and a nice list of toxins and effects is provided at the end of the chapter. Laboratory safety is well done in chapter three covering documentation, problem chemical classes, containers, storage and handling. Personal protection equipment (PPE) for laboratories is briefly described. This chapter will benefit those focusing on basics of laboratory safety in smaller operations.

Chapter four entails Resource Conservation and Recovery Act (RCRA) and Waste Analysis Plans, Waste Classification per EPA, generators and laboratory regulations, ending with Waste Analysis Plan requirements. Hazard Communication including training and detailed labeling requirements is detailed in Chapter 5. The forms and identities of hazards and exposure are discussed along with prevention of exposure. The chapter closes on ventilation requirements and a brief section on radiation hazards.

Chapter six looks at process safety and hazard analysis again with chemical description requirements, etc., and then into requirements expected for process equipment (ANSI, ASTM, etc.). The balance of the chapter is a clear view at conducting a process hazard analysis, dealing with the results, and other details of hazardous operations (HAZOP).

Chapters seven, eight and nine focus on hazardous waste transportation regulations, waste minimization for facilities, and underground storage tanks, respectively. Each chapter looks at regulations and requirements for the subject. Corrective actions and preventive measures for leaking underground storage tanks (LUST) problems are also included in chapter nine. Chapter ten deals with the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and is a

fairly brief discussion focusing on pesticides and use/storage requirements. Chapter eleven ends the text with a very well done personal protective equipment (PPE) presentation. This is an excellent resource for those training or routinely using PPE. The discussion is very organized and includes stress problems in PPE use. The index for the text is sufficient for topic location.

This text should serve as a useful reference for professionals in training and compliance in industry with the number of topics provided in eleven clearly written chapters. In such a broad field as safety management for hazardous materials, they have done a very good job to bring salient topics together in one book.

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POLLUTION PREVENTION SOFTWARE SYSTEMS HANDBOOK

Michael F. Wood, John A. King, and Nicholas P. Cheremisinoff, Noyes Data Corporation, Westwood, NJ, (1997), 521 pages, [ISBN No.0-8155-1405-0], U.S. List Price: \$84.00

This book discusses software systems that an engineer, pollution prevention specialist, or a system planner could use in the execution of their function. Divided into ten chapters the book details specific types of software covering the range from cost estimating tools, schedule and control, risk assessment, remediation, tracking, financial analysis, cost impact, to waste reduction programs. Each chapter presents an evaluation of several different software systems.

Descriptions of individual software systems are very detailed. The description summarizes the software and its applicability, basic support system requirements, availability (some of the systems are not available to the public), and cost. The book goes to great lengths to describe applicability, methodology, advantages, and liabilities of each system. The discussion is particularly valuable for comparing and evaluating different types of programs and their specific uses prior to testing or purchase.

The book discusses a number of software packages in each different area ranging from the high end programs with many options down to smaller scale programs that would find their advantage in smaller projects or programs. For instance the book discusses thirteen, cost and schedule packages ranging from Primavera Project Planner at the high end to Forefront on the abbreviated profiles. The description of each software package is very detailed and is of use to the potential software user and system programmer.

The handbook has particular value to engineers and professionals who are searching for software systems to fill a particular need. The detailed technical descriptions and evaluation of technical capabilities and requirements of each system are invaluable for making preliminary assessments of software products and assessing compatibility with existing systems, programs, and software configurations. The discussion can limit the number of potential choices down to one or two that can meet a particular need. This will minimize the need to try many different programs that can waste resources.

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A Review of Heating and Ventilation Web Sites on Internet

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INTRODUCTION

Environmental issues like global warming, caused in part as a result of burning fossil fuels, ozone depletion affected by the efficiency of energy usage, indoor air quality, all come to a root concern involving energy usage. The heating and ventilation discipline deals with this issue of energy usage, to arrive at systems that are not only energy efficient but also environment friendly [1]. The constant demand for energy conservation and good indoor air quality invites technological innovation to improve system efficiencies and to efficiently maintain existing systems. Heating and ventilation engineers are working closely with health professionals to develop systems for removing harmful chemicals and biological agents from building air systems.

Industrial ventilation is of utmost importance to environmental professionals primarily due to the fact that it determines the health and safety of the workers in the industry [2]. The concept of industrial ventilation covers a very broad spectrum of topics, from the design of the simple domestic system, to sophisticated control systems for industrial processes. Designing for optimum ventilation performance is a vital part of building design, and the Internet is a useful repository of information that can help the professionals in developing systems that are cost effective and advanced in design and functioning. Heating and ventilation systems increasingly are becoming the key to maintaining acceptable environmental standards. Information on various issues of industrial ventilation is required at every point of plant operation and the Internet provides us with easy access to the necessary information.

In the recent times, the Internet has moved from being a mere curiosity to being a technology asset. It now allows us to disseminate much more information to a wide number of constituents. The Internet is a means of communication, an informa-

tion resource that has literally millions of computers packed to the hilt with documents, graphics, and other information resources. It is also a warehouse storing thousands of files to be retrieved when needed. Internet essentially organizes information and provides a space for sharing ideas, giving universal access independent of physical location [3]. There is no wonder that the Internet holds such a fascination for computer pros and amateurs alike. The print and electronic sources are exploiting technologies such as Internet providing greater options for information sharing. Internet enables us to have the panoramic views and outlooks of different people thus acting as a bridge to link with others in successfully dealing with the issues and create innovative solutions. Thus it is logical to conclude that only dynamic, forward looking and globally oriented environmental professionals aided by up to minute information generated globally can provide quality service in the realm of continuously changing specialized information needs and participate in exchange of information on global developments and professional issues related to heating and ventilation.

To surf the net one can use many search engines which help in querying the required topic and opens before us an information galaxy to choose from. Many search engines that collect the databases based on query word(s) given to them are available of which Lycos, Infoseek, Webcrawler, Excite, Yahoo are some to be named. Input words like 'HVAC' or 'industrial ventilation', in the word search of any Internet search engine will result in links to sites that contain topics related to the search item. This process can turn out to be laborious at times as all the sites that are even vaguely related to the search items will show up. One way to limit this is to insert the search word(s) within inverted comma " ", which results in the

exhaust of not so specific sites. But even then you may miss out on an informative site if you are in a haste to obtain the desired information. The other way to access any site is to plug in the site URL (Uniform Resource Locator—a web addressing scheme that spells out the exact location of a Net resource), if known, in an Open Location field of your Internet browser [4].

This paper provides you with a list of URL's of web sites related to heating and ventilation. We reviewed these Internet sites and found them to be informative. A brief description for each site is provided in this paper, to help you find what you are looking for. All you need to do is type in the web site URL in the 'Open Location' field of your Internet browser and GO.

HEATING AND VENTILATION WEB SITES

• Air Conditioning Contractors of America <http://www.acca.org/>

Air Conditioning Contractors of America (ACCA) is a national trade association which represents heating, ventilation, air conditioning, and refrigeration (HVAC&R) companies which design, install, maintain, and service HVAC&R systems. ACCA members work on all kinds of systems including residential, commercial, industrial, institutional, and governmental. The ACCA web page provides management, technical, and educational information including articles, and product information. The site contains information on the various chapters within the organization, and also includes an on-line membership form. ACCA's members include manufacturers of HVAC&R equipment, wholesalers and distributors, vocational and technical schools, and others. The association advocates the concerns of HVAC&R contractors in the United States Congress and federal regulatory agencies, and also provide information to ACCA members and chapters about legislation and regulations that affect their businesses.

• Air Handling Systems <http://www.cybermarf.com/airhand/>

This internet catalog is a source for dust collection and ventilation needs, and provides information about many of the popular air handling systems products. One can find information about designing your own dust and fume collection systems and the installation of spiral pipes and fittings. The page also contains product information on welded elbows, tees, Y branch/45 degree tee on taper, spun, reducers/bellmouths, saddle tap tee/hangers, gates, and hoses.

• **Air Infiltration and Ventilation Center**
<http://www.aivc.org/>

The Air Infiltration and Ventilation Center (AIVC) provides technical support to those involved in the research and development of ventilation technology. The Center provides a comprehensive information service, and their page on the net gives information on related energy and air quality issues. AIRBASE, the bibliographic database of the International Energy Agency's Air Infiltration and Ventilation Center contains abstracts of articles, and other publications related to energy efficient ventilation and associated issues. AIVC's numerical database contains air exchange rates which are particularly applicable to the evaluation of construction design, ventilation strategies, energy impact of ventilation, the performance of standards and recommendations, and the influence of climate and calculation techniques. In addition one can find the World Wide Web edition of "Air Infiltration Review (AIR)," a quarterly newsletter of information, news and short technical items on air infiltration research and application.

• **American Conference of Governmental Industrial Hygienists (ACGIH)**
<http://www.ACGIH.org/>

The ACGIH web site is a helpful resource for professionals interested in the field on occupational safety and health. The site provides visitors with an overview of the ACGIH journal, 'Applied Occupational and Environmental Hygiene', along with categorical indexing of the over 350 publications offered by organization. Condensed versions of many of the articles from "Today", the newsletter published by ACGIH, are also posted on the page. The web site gives latest information on upcoming conferences, training courses, and other special events sponsored by ACGIH. A service provided through this site allows concerned individuals to pose, answer, or discuss scientific or technical questions, and issues related to occupational health and safety [5].

• **American Gas Cooling Center**
<http://www.agcc.org/>

American Gas Cooling Center's Web site is designed to provide you access to natural gas air conditioning, dehumidification, and refrigeration information, technologies and applications. The AGCC is funded by the natural gas industry and heating, ventilation, and air conditioning equipment manufacturers to facilitate the commercialization of natural gas cooling and heat pump equipment.

• **Air-Conditioning & Refrigeration Institute**
<http://www.ari.org/>

The Air-Conditioning and Refrigeration

Institute (ARI) is a voluntary, nonprofit organization comprised of the manufacturers of air conditioning, refrigeration, and heating products. ARI develops and publishes technical standards for industry products. ARI maintains an extensive library of publications containing topics of interest to the HVAC&R industry. The site contains links to consumer brochures, ARI standards and guidelines, unitary and applied directories, list/links of ARI member companies, issues affecting the HVAC&R industry, government affairs, international trade program, research and technology program, and the ARI refrigerant database education program.

• **ASHRAE**
<http://www.ashrae.org/>

ASHRAE, the American Society of Heating, Refrigerating and Air-Conditioning Engineers is an international organization for advancing the arts and sciences of heating, ventilation, air conditioning and refrigeration for the public's benefit through research, standards writing, continuing education and publications. ASHRAE writes standards that set uniform methods of testing and rating equipment and establish accepted practices for the HVAC&R industry worldwide, such as the design of energy efficient buildings. The organization web site gives link to the on-line edition of the ASHRAE journal. This WWW edition of the journal provides HVAC&R product literature and information, news, and publications comprising of technical features, abstracts from the research journal, and technology questions and answers. Corrections to ASHRAE handbook are also listed at this link. The research and standards link on the web site documents the ASHRAE guideline 1 through 58, and the ASHRAE standards 62 through 161. The latest information on upcoming meetings, and conferences, student activities, and continuing education is also provided on the organization web page. The ASHRAE bookstore catalog lets you order on-line codes, data, manuals, guidelines, handbooks, and standards, and also provides a brief introduction to information contained in these publications.

• **Carrier Corporation**
<http://www.carrier.com/>

The resource center page of Carrier Corporation, maker of air conditioning, heating, refrigeration and ventilation equipment, gives common information about HVAC and related industries. The page contains a glossary of commonly used terms, case studies, white papers, and carrier software information. The carrier homepage also contains useful information on comfort at home, and at work, including a link for FAQ's

• **Delta-Therm Corporation**
<http://www.delta-therm.com/>

Delta-Therm Corporation designs, manufactures, and sells high quality heat transfer components. The company home page contains information on the various applications including earth thermal storage, floor warming, hangar door rail deicing, permafrost prevention, pipe tracing, process heating, roof and gutter deicing, and snow melting. Delta-Therm's on-line technical library includes technical bulletins, and installation instructions which can be viewed using the Adobe Acrobat reader software.

• **Elite Software**
http://www.elitesoft.com/elite_hvac_ndx.html/

Elite Software's HVAC&R programs web site provides software product information for such computer software applications as HVAC load calculations, building energy analysis, duct design, ground source pipe loop sizing, chilled and hot water analysis for HVAC piping systems, and some miscellaneous programs for gas vent sizing, psychometric analysis, U-Factors, and HVAC estimation and sales.

• **EPRI HVAC&R Center**
<http://www.engr.wisc.edu/centers/tsarc/tsarc.html>

EPRI HVAC&R center is an EPRI sponsored technology center located in the college of engineering at the University of Wisconsin-Madison. The center provides direct support to EPRI-member utilities, including telephone consultation, technology transfer products, seminars and workshops, and involvement in collaborative research projects with EPRI. The Center solicits advice and technical guidance from a broad array of utility personnel, manufacturers, government agencies, design professionals, and end-users through several processes, including advisory councils and expert workshops. The Center is actively involved in ASHRAE, which helps EPRI to maintain a high profile within this organization. An on-line edition of the newsletter published by the EPRI HVAC&R center can be accessed through the web site.

• **Greenhouse Ventilation**
<http://hammock.ifas.ufl.edu/txt/fairs/1817>

This document is a series of fact sheets developed by the Agricultural Engineering Department, University of Florida. The fact sheets contain information about greenhouse ventilation during winter, summer, spring, and fall, determining ventilation volume rates, air distribution within greenhouses, and natural ventilation.

• **Hitching Associates, PC**
<http://www.safelab.com/>

HAPC is an engineering and industrial

hygiene consulting firm specializing in laboratory planning, safety and design, ASHRAE 110 fume hood testing, industrial ventilation, and indoor air quality. The technical resources section of the web page of the firm provides fact sheets, technical publications, and design aids related to industrial ventilation. One can also find information on HAPC projects, and client services provided by the firm.

• **HVAC Engineering Programs: Written by Randall C. Wilkinson**
<http://www.iar.com/~randyw/engproj.html>

These HVAC engineering programs, written by Randall C. Wilkinson are available for download on his personal web page. The programs that can be found here help in designing and drawing 2D, 2-line heating and air conditioning ducts, Duct Sizing, Pipe Sizing, Building Heating Load, Psychometric Functions. A duct sizing calculator is also available for download.

• **HyCal**
<http://www.hycalnet.com/HVAC/index.html>

Hycal designs and manufactures advanced building and environmental control sensors and transmitters, that help you to monitor and measure temperature, moisture, and CO₂ for the precise control of indoor air quality. The company web site provides technical product information on temperature sensors, humidity & temperature transmitters, dew point, enthalpy or wet-bulb transmitter with dry-bulb temperature, and CO₂ transmitter.

• **Hy-Save, Inc.**
<http://www.hysave.com/>

These pages will tell you about Hy-Save's energy conservation technologies for refrigeration and air conditioning systems. Information can be found on Hy-Save Liquid Pressure Amplifier Technology, and the Hy-Dry Subcooling-Reheat Dehumidification Technology.

• **Industrial Ventilation Development Program (INVENT)**
<http://www.invent.hut.fi/index.html>

The Industrial Ventilation Development Program (INVENT) is a five-year technology program started by the Finnish ventilation industry, and research institutes. The program aims to systematically promote the development of industrial ventilation by improving the technological level of equipment and systems. The INVENT web site reports on current issues dealing with the industrial ventilation program. An overview of 'Industrial Air Quality', 'Industrial Air Technology Design Guide Book', and research projects at INVENT is provided on the site. The publications link at the web site provides the summary of reports on current issues dealing with the industrial ventilation technology program.

• **Jetfan Technology**
<http://www.ozemail.com.au/~jetfan/>

JETFAN Technology is a research and development company that licenses its technology to manufacturers. The company home page contains an insight into the Jetfan, its applications, and also information on the conventional fans including axial flow fans, centrifugal radial fans, mixed flow fans.

• **Lawrence Livermore National Laboratory**
http://www.llnl.gov/es_and_h/hsm/chapter_12/chap12.html

Chapter 12 of LLNL's Health & Safety Manual covers the topic of Ventilation, and provides general information on ventilation systems.

• **Nautica Dehumidifiers, Inc.**
<http://www.gw2.com/nautica/>

The web site for Nautica Dehumidifiers Inc., producers high latent air conditioning, and dehumidification equipment gives information about its refrigerated dehumidifiers utilizing plate heat exchangers, the thermodynamic and equipment configurations, and its applications.

• **Radiant Panel Association**
<http://www.rpa-info.com/>

The Radiant Panel Association (RPA) home page provides some basic information about radiant heating, how it works, where it is used, how it is installed as well as comfort and efficiency.

• **Resources for Environmental Design Index (REDI)**
<http://www.oikos.com/cgi-bin/redi/menu.pl?topic=Mechanical/>

The Oikos Product Gallery displays a selection of new or unique products. The 'Mechanical' helps you find companies that carry equipment's in the following categories: Air Cleaning Devices, Cooling, Ductwork and Accessories, Heat Pumps, Heating, HVAC Controls, Indoor Ventilation, Plumbing, Structural Ventilation, and Water Heaters.

• **Refrigeration Service Engineers Society (RSES)**
<http://www.rses.org/>

Refrigeration Service Engineers Society (RSES) is a non-profit international association whose 35,000 members install, service, and repair HVAC and refrigeration systems. The society provides training and education for its members through locally led courses, periodic service bulletins, and the monthly RSES Journal. The society publishes a sample article from the RSES journal on their page. Information can be obtained on membership, seminars, and other upcoming events.

• **Solstice, Heating, Ventilation, and Air-Conditioning**
<http://www.crest.org/environment/gotwh/general/menus/html/heating-cooling.html>

Solstice, the site for energy efficiency, renewable energy, and sustainable technology information and connections, covers topics related to heating, ventilation, and air-conditioning. The residential heating and cooling section provides useful information on weatherization, types of system, and selecting, replacing, and locating your system. The HVAC controls section gives information on use of controls to regulate the amount, timing, and distribution of heating and cooling, and covers the topics on residential HVAC zoning, programmable thermostats, and mercury in thermostats.

• **Standards-Based Management Systems (SBMS): Using Local Exhaust Ventilation**
<http://sbms.pnl.gov:2080/standard/Oy/Oy00010.htm>

Information can be retrieved from this site on planning to use a local exhaust ventilation device, using a local exhaust ventilation device, factors to evaluate when selecting a local exhaust ventilation device, guidelines for emergency situations and response actions, operational checks of the local exhaust ventilation device, and some useful definitions.

• **Sci. Engr. Heat-Vent-AC Frequently Asked Questions**
<http://www.elitesoft.com/sci.hvac/>

This is the World Wide Web FAQ section for 'sci.engr.heat-vent-ac', the usenet newsgroup for the Heating, Ventilating, and Air Conditioning (HVAC) industry.

• **SunNorth Systems Ltd.**
<http://www.SunNorth.com/>

Sun-North offers a wide range of natural ventilation products. The page provides a short summary on natural ventilation, and its advantages over other systems. The site also includes pages for all the different products offered by SunNorth, and contains a detailed list of their key features.

• **Taco-HVAC**
<http://www.taco-hvac.com/>

Taco, Inc. is a leading developer and supplier of hydronic-based heating and cooling components for both residential and commercial applications. The home page for Taco Inc. offers information in the adobe acrobat reader format on their complete line of products utilized in commercial and residential HVAC Systems, and also the fabricated products. The web site also provides information on TacoNet, a complete software package designed to make it easier to select, specify and apply Taco Products. The software is designed for use on stand alone MS-DOS Pcs or

network applications. The software includes product selection programs, a complete set of guide specifications for all Taco products and a library of AutoCAD compatible product installation drawings. Equipment selections are many simply with minimal input and link directly to the users drawings through AutoCAD compatible schedule files.

• **Trane**
<http://www.trane.com/>

The Trane company is a worldwide manufacturer of heating, ventilation, air conditioning, and building management equipment, and systems, which include central station air handlers, variable air volumes systems, commercial rooftop systems, integrated comfort systems, and centrifugal chillers. Trane offers a toolbox of software to help you design, size, select, and apply equipment in heating, ventilation and air-conditioning systems for all types of buildings. The page provides information about their analysis, design, economic, and equipment selection tools. The Trane company web site provides information about their comfort systems for residential, commercial, institutional and industrial buildings, and also equipment used in industrial process applications. The Earth issue link on the company web page discusses the issues of energy,

CFC, indoor air quality, and the associated laws, standards, and regulations. The adobe acrobat versions of their engineers newsletter is also on-line, and a few case studies are provided.

• **York International Corporation**
<http://www.york.com/>

York designs, manufacturers, sells and services heating, ventilation and air conditioning systems and compressors for residential and commercial markets, gas compression equipment for industrial processing, industrial and commercial refrigeration equipment, and compressors for air conditioning and refrigeration applications. The web site for York International Corporation offers information on industry issues, including indoor air quality, energy efficiency, natural gas cooling, and replacement. The information is organized into three groups, commercial, residential, and refrigeration.

CONCLUSIONS

On-line information on heating and ventilation can now be accessed on the World Wide Web through the web sites maintained by organizations such as ACCA, AIVC, ARI, ASHRAE, and through the web pages of commercial companies dealing with heating and ventilation.

The web site addresses for the 30 Internet sites listed in this paper will help

reduce the time for the reader to search for the required information. We suggest the concerned individuals to regularly check the 'What's New' section in these Internet sites where applicable. This section in the web sites is constantly updated. The latest highlights and information on the heating and ventilation industry is also published. We hope that the reader can use this paper as a reference guide to find material for their use.

REFERENCES

1. Patterson, N., D. Flamm, "The Industry Challenges Ahead in 1994", *ASHRAE Journal*, Vol. 36, pp. S15-20 (January 1994).
2. Kumar, A., S. Vashisth, F. D'souza, "Introduction to WWW.Environment_Health & Safety.Com", *Environmental Progress*, Vol. 15(4), pp. W13-16 (Winter 1996).
3. Earnshaw, R., "3-D and Multimedia on the Information Superhighway", *IEEE Computer Graphics and Applications*, pp. 30-31 (March/April 1997).
4. Kumar, A., S. Vashisth, F. D'souza, "Environmental Datasets on the Information Superhighway", *Environmental Progress*, Vol. 15(3), pp. F13-16 (Fall 1996).
5. Daniels, W., S. Salisbury, "The ACGIH Web Site," *Applied Occupational and Environmental Hygiene*, Vol. 12(2), pp. 97-98 (February 1997).

Escalating Air Pollution Control Equipment Costs

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INTRODUCTION

Reliable air pollution control equipment cost data are hard to obtain. Even rarer are costs that are both reliable and current. Consequently, the analyst needing to make control cost estimates—control agency engineer, company manager, university professor, doctoral student—has had to adjust (“escalate”) the data he/she is able to obtain to a different date, usually the present. Until recent years, these equipment cost escalations have had to be made using various standard indexes, such as the Marshall and Swift (M&S) Equipment Cost Index and the Chemical Engineering Plant Index (CEPI). No published indexes specific to air pollution control equipment were available.

To fill this “data vacuum,” we developed just such a set of cost indexes, each designed for a particular category of control equipment. Collectively named the “VAPCCI” (for Vatavuk Air Pollution Control Cost Indexes), these quarterly indexes cover eleven equipment categories:

- Carbon adsorbers
- Catalytic recuperative incinerators
- Electrostatic precipitators
- Fabric filters
- Flares
- Gas absorbers
- Mechanical collectors
- Refrigerated condensers
- Regenerative thermal oxidizers
- Thermal recuperative incinerators
- Wet scrubbers

For two of the categories (mechanical collectors and fabric filters), the VAPCCI were based on Producer Price Indexes (PPI) developed for them by the U.S. Department of Labor’s Bureau of Labor Statistics (BLS).³ The monthly PPI’s for these two devices were averaged for a given quarter and reported. The other nine VAPCCI

CI, however, were computed via a special procedure. The procedure used to develop these VAPCCI and the data inputs underlying them are thoroughly described in a U.S. Environmental Protection Agency report, *Escalation Indexes for Air Pollution Control Costs* (EPA-452/R-95-006). This article summarizes this procedure and presents VAPCCI data from the initial date (first quarter 1994) through the present (first quarter 1997).

BUILDING THE VAPCCI

Like other escalation indexes, the VAPCCI are simple to use. To escalate a cost from one date (initial) to another (final), use the following equation:

$$\text{COST}_{(\text{final})} = \text{COST}_{(\text{initial})} \left[\frac{\text{VAPCCI}_{(\text{final})}}{\text{VAPCCI}_{(\text{initial})}} \right] \quad (1)$$

Problem: A cost of a recuperative thermal incinerator when purchased and installed in first quarter 1994 is \$56,000 (rounded to nearest \$100). What would this cost be when escalated to third quarter 1996 dollars?

Solution: The thermal incinerators VAPCCI for third quarter 1996 and first quarter 1994 (the indexes’ start date) are 108.3 and 100.0, respectively. Substituting these values and the cost into the equation above, we obtain:

$$\begin{aligned} \text{COST}(\text{third quarter 1996}) \\ = \$56,000 \times (108.3/100.0) = \$60,600. \end{aligned}$$

As this example shows, each VAPCCI value is rounded to the nearest tenth, with a base value of 100.0 (corresponding to the base date of first quarter 1994).

Except for fabric filters and mechanical collectors, each VAPCCI is computed using a weighting scheme that is based on: (a) the PPI (and, where applicable, the BLS

Employment Cost Index element (ECI) for the several components making up the control device and (b) the “cost weighting factors”—the fraction of the total (list) equipment price to which each of these components contributes. The following equation illustrates this calculation for any of the nine control devices:

$$\text{VAPCCI}_q / \text{VAPCCI}_b = \sum_{j=1}^n (\text{CWF}_j) \left(\frac{\text{PPI}_q}{\text{PPI}_b} \right)_j \quad (2)$$

where:

$\text{VAPCCI}_q / \text{VAPCCI}_b$ = ratio of the VAPCCI’s for the quarter of interest and the base quarter (1st quarter 1994), respectively

CWF_j = cost weighting factor for component “j” (of “n”)

$(\text{PPI}_q / \text{PPI}_b)_j$ = ratio of producer price indexes (quarterly averages) for component “j”

To obtain the VAPCCI for the quarter of interest (“q”), multiply the result from equation (2) by VAPCCI_b (=100.0), or:

$$\text{VAPCCI}_q = 100.0 \times (\text{VAPCCI}_q / \text{VAPCCI}_b) \quad (3)$$

As mentioned above, the PPI’s/ECI’s for a given control device category were obtained from the Bureau of Labor Statistics. But *which* of the thousands of PPI’s reported were selected for which control device components? In making these selections, we first reviewed the list of device components and tried to match each to a specific PPI. Successful matches were found for such components as fans, motors, pumps, and burners—components that typically are manufactured by suppliers and connected to the control device by the vendor. Many PPI’s were selected in this way.

For those components where PPI matches could not be made, we chose “surrogate” PPI’s. For instance, as a surrogate for the electrodes and collecting plates of an electrostatic precipitator—an essential component of that device—we selected the PPI for “sheets, hot rolled, carbon” (PCU3312#311). We reasoned that the plates in a typical ESP would be fabricated of carbon steel sheet and that changes in ESP plate prices would track the price changes in this material.

³These PPI are: fabric filters—PCU 356#65113; mechanical collectors—PCU 356#65115. For more information about the thousands of PPI computed and published, consult: *BLS Handbook of Methods*, Bureau of Labor Statistics, U.S. Department of Labor, Washington, D.C. 1992.

²Copies of this report are available from EPA’s Office of Air Quality Planning and Standards (OAQPS) Technology Transfer Network (TTN) on the Internet. The website address: [HTTP://TINWWW.RTP.NC.EPA.GOV](http://ttnwww.rtp.nc.epa.gov).

Next, these PPI's were "married" to the component cost weighting factors, as shown in equation (2). The weighting factors were obtained from a survey of control equipment vendors. In this survey, we asked vendors to provide weighting factors for three size ranges for each control device: "Small," "Medium," and "Large". The size ranges varied according to control device. For instance, for gas absorbers, the ranges were: Small—<2,000 acfm (actual cubic feet per minute) of waste gas flow; Medium—2,000 to 40,000 acfm; Large—>40,000 acfm. The size-specific cost weighting factors for all of the control device categories except ESP's are presented in the EPA report, *Escalation Indexes for Air Pollution Control Costs*.

Because the ESP vendors were not surveyed until after this report was released, the ESP data were not included therein. For the sake of completeness, the ESP cost weighting factors are presented in this article, along with the corresponding PPI's and the ECI element (used for the "engineering and project" cost component). These data are listed in Table 1. Note that the single largest contributor to the cost of the "medium" and "large" units is the ESP casing, while for the "small" unit, the engineering and project cost accounts for the biggest fraction. The collecting plate areas corresponding to these size categories are listed in Table 1.

THE VAPCCI TO DATE:

The VAPCCI have been disseminated via the OAQPS TTN since fall 1995. The indexes are contained in a series of "updates," the latest being the sixth.^a Because the size-specific indexes are so voluminous, there is not enough space to reproduce all of the VAPCCI from first quarter 1994 to the present. These indexes are posted on the TTN. In this article we will show both the size-specific and the average VAPCCI from first quarter 1996 through first quarter 1997 (preliminary).^b **The VAPCCI for first quarter 1997 (final) and subsequent quarters will be published in future issues of *Environmental Progress*.**

The VAPCCI for these five quarters are shown, successively, in Tables 2 through 6. For each of the nine control devices, each table lists both the size-specific VAPCCI and

^aThe TTN file names of the latest (sixth) update are "ESCA-UP6.WP5" (WordPerfect 5.1 format) and "ESCA-UP6.TXT" (ASCII format). In addition, updates 1 to 5 have been compressed into a single file, "UP1-5.ZIP".

^bPreliminary VAPCCI are reported for a given quarter when their PPI and/or ECI inputs are only available in preliminary form. Once the final inputs are released by the BLS, the VAPCCI are finalized.

Table 1. Electrostatic Precipitator Components: Price Indexes and Cost Weighting Factors*

Component	Price Index (number)	Cost Weighting Factor		
		Small	Medium	Large
ESP casing	Plates, carbon (PCU3312#412)	0.255	0.338	0.395
Dust hoppers	Plates, carbon (PCU3312#412)	0.076	0.071	0.101
Electrodes and plates	Sheets, hot rolled carbon (PCU3312#311)	0.051	0.133	0.163
Transformer rectifier sets and controls	Rectifying apparatus, except electronic (PCU3629#2)	0.093	0.091	0.078
Rappers	Other power transmission equipment, except aircraft, automobile, (PCU3568#3g)	0.000	0.027	0.023
Insulation	Mineral wool for industrial & equipment insulation (WPU139202)	0.077	0.058	0.057
Instrumentation	Process control instruments (WPU1182)	0.120	0.080	0.031
Supports and access	Bars, light structurals, carbon (PCU3312#424)	0.064	0.083	0.065
Engineering and project	Employment Cost Index professional specialty & technical (ECU111221)	0.263	0.114	0.087

*The size categories shown in this table correspond to the following ESP collecting plate areas:

Small—<10,000 ft²
 Medium—10,000 to 50,000 ft²
 Large—>50,000 ft²

the arithmetic average of these values. To give some notion of the sensitivity of the VAPCCI with device size, a statistic—the "range/average" (R/A)—was defined. This is as follows:

$$R/A = \frac{(\text{VAPCCI}_{\text{highest}} - \text{VAPCCI}_{\text{lowest}})}{|\text{VAPCCI}_{\text{average}} - 100.0|} \quad (4)$$

where: $\text{VAPCCI}_{\text{highest/lowest}}$ = the highest and lowest indexes for the three size categories, respectively.

Note that the denominator of equation (4) is expressed as the *absolute* value of the difference between the average VAPCCI and 100.0 (the VAPCCI baseline). The absolute value is taken because, if the PPI/ECI inputs should drop below January 1994 levels, the VAPCCI computed from them could be less than 100.0

The R/A's vary noticeably by quarter and control device category. Over these

five quarters, carbon adsorbers, flares, and wet scrubbers generally have had the largest R/A's; thermal incinerators, regenerative thermal oxidizers, and refrigerated condensers, the smallest. Also, the R/A's have tended to decrease during this period. The R/A's for first quarter 1996 ranged from 4.3 to 49.2%, while for first quarter 1997, the range in this statistic was much smaller: 4.0 to 17.6%. This R/A trend reflects both the differences in the control device cost weighting factors and the price histories of the ECI and the various PPI inputs to the VAPCCI.

Finally, Table 7 lists the average VAPCCI for the nine control devices, plus fabric filters and mechanical collectors. These are given for these five quarters and for the years 1994 and 1995. The 1994-95 VAPCCI are arithmetic averages of the four quarterly values for each year.

Table 2. Vativuk Air Pollution Control Cost Indexes: First Quarter 1996 (Final)

Control Device	VAPCCI by Size Category (First Quarter 1994 = 100)				
	Small	Medium	Large	Average ^a	Range/Average × 100% ^b
Carbon adsorbers	107.44	110.00	110.13	109.19	29.3
Catalytic incinerators	107.45	107.77	107.78	107.67	4.3
Electrostatic precipitators	106.97	106.53	107.41	106.97	12.6
Flares	105.76	104.30	103.53	104.53	49.2
Gas absorbers	108.52	109.14	108.15	108.60	7.2
Refrigeration systems	104.09	104.11	104.39	104.20	7.1
Regenerative thermal oxidizers	105.51	105.99	105.99	105.83	8.2
Thermal incinerators	107.81	107.88	108.15	107.95	4.3
Wet scrubbers	110.25	111.78	113.06	111.69	24.0

^a Arithmetic averages of the three VAPCCI values.

^b Calculated as follows:

$$R/A = (High\ Index - Low\ Index) / |Average\ index - 100| \times 100\%$$

Table 3. Vativuk Air Pollution Control Cost Indexes: Second Quarter 1996 (Final)

Control Device	VAPCCI by Size Category (First Quarter 1994 = 100)				
	Small	Medium	Large	Average ^a	Range/Average × 100% ^b
Carbon adsorbers	106.15	108.17	108.23	107.51	27.7
Catalytic incinerators	106.95	107.08	106.96	106.99	1.9
Electrostatic precipitators	107.51	107.14	108.18	107.61	13.7
Flares	105.75	104.75	104.21	104.90	31.4
Gas absorbers	108.07	108.69	107.78	108.18	11.1
Refrigeration systems	104.01	104.05	104.38	104.15	8.9
Regenerative thermal oxidizers	105.70	106.21	106.15	106.02	8.5
Thermal incinerators	107.88	107.93	108.24	108.02	4.5
Wet scrubbers	109.00	110.20	111.00	110.07	19.9

^a Arithmetic averages of the three VAPCCI values.

^b Calculated as follows:

$$R/A = (High\ Index - Low\ Index) / |Average\ index - 100| \times 100\%$$

Table 4. Vativuk Air Pollution Control Cost Indexes: Third Quarter 1996 (Final)

Control Device	VAPCCI by Size Category (First Quarter 1994 = 100)				
	Small	Medium	Large	Average ^a	Range/Average × 100% ^b
Carbon adsorbers	104.28	105.66	105.64	105.19	26.6
Catalytic incinerators	107.13	107.15	106.94	107.07	3.0
Electrostatic precipitators	108.54	108.45	109.69	108.89	13.9
Flares	105.69	104.98	104.57	105.08	22.0
Gas absorbers	106.91	107.39	106.87	107.06	7.4
Refrigeration systems	104.33	104.38	104.62	104.44	6.5
Regenerative thermal oxidizers	106.36	106.86	106.78	106.67	7.5
Thermal incinerators	108.21	108.27	108.55	108.34	4.1
Wet scrubbers	108.50	109.46	109.95	109.30	15.6

^a Arithmetic averages of the three VAPCCI values.

^b Calculated as follows:

$$R/A = (High\ Index - Low\ Index) / |Average\ index - 100| \times 100\%$$

Table 5. Vatavuk Air Pollution Control Cost Indexes: Fourth Quarter 1996 (Preliminary)

Control Device	VAPCCI by Size Category (First Quarter 1994 = 100)				
	Small	Medium	Large	Average ^a	Range/Average × 100% ^b
Carbon adsorbers	103.52	104.14	104.03	103.90	15.9
Catalytic incinerators	106.03	105.89	105.59	105.84	7.5
Electrostatic precipitators	108.05	107.88	108.95	108.29	12.9
Flares	106.11	105.63	105.36	105.70	13.2
Gas absorbers	106.74	107.26	106.68	106.89	8.4
Refrigeration systems	104.70	104.76	105.06	104.84	7.4
Regenerative thermal oxidizers	106.18	106.68	106.62	106.49	6.8
Thermal incinerators	108.06	108.12	108.40	108.19	4.2
Wet scrubbers	108.37	109.16	109.39	108.97	11.4

^a Arithmetic averages of the three VAPCCI values.

^b Calculated as follows:

$$R/A = [(\text{High Index} - \text{Low Index}) / (\text{Average index} - 100)] \times 100\%$$

Table 6. Vatavuk Air Pollution Control Cost Indexes: First Quarter 1997 (Preliminary)

Control Device	Equipment Cost Index (First Quarter 1994 = 100)				
	Small	Medium	Large	Average ^a	Range/Average × 100% ^b
Carbon adsorbers	103.70	104.43	104.31	104.15	17.6
Catalytic incinerators	105.96	105.64	105.23	105.61	13.0
Electrostatic precipitators	108.64	108.38	109.40	108.81	11.6
Flares	105.77	105.44	105.28	105.49	8.9
Gas absorbers	108.53	109.14	108.32	108.66	9.5
Refrigeration systems	104.95	105.05	105.24	105.08	5.7
Regenerative thermal oxidizers	107.00	107.44	107.36	107.27	6.1
Thermal incinerators	108.92	108.97	109.28	109.06	4.0
Wet scrubbers	108.06	108.54	108.41	108.34	5.8

^a Arithmetic averages of the three VAPCCI values.

^b Calculated as follows:

$$R/A = [(\text{High Index} - \text{Low Index}) / (\text{Average index} - 100)] \times 100\%$$

Table 7. VAPCCI Summary

Control Device	VAPCCI Air Pollution Control Cost Indexes (1st quarter 1994 = 100.0) ^a						
	1994-avg ^b	1995-avg ^b	1st Q'96	2nd Q'96	3rd Q'96	4th Q'96 ^c	1st Q'97 ^c
Carbon adsorbers	101.2	110.7	109.2	107.5	105.2	103.9	104.2
Catalytic incinerators	102.0	107.1	107.7	107.0	107.1	105.8	105.6
Electrostatic precipitators	102.8	108.2	107.0	107.6	108.9	108.3	108.8
Fabric filters ^d	100.5	102.7	104.0	104.2	104.8	105.0	105.3
Flares	100.5	107.5	104.5	104.9	105.1	105.7	105.5
Gas absorbers	100.8	105.6	108.6	108.2	107.1	106.9	108.7
Mechanical collectors ^d	100.3	103.0	103.3	103.3	103.3	103.3	103.5
Refrigeration systems	100.5	103.0	104.2	104.2	104.4	104.8	105.1
Regenerative thermal oxidizers	101.4	104.4	105.8	106.0	106.7	106.5	107.3
Thermal incinerators	101.3	105.9	108.0	108.0	108.3	108.2	109.1
Wet scrubbers	101.3	112.5	111.7	110.1	109.3	109.0	108.3

^a Except for fabric filters and mechanical collectors, each value shown is the arithmetic average of the size-specific VAPCCI, rounded to the nearest tenth.

^b Arithmetic average of quarterly VAPCCI for year indicated.

^c All fourth quarter 1996 and first quarter 1997 VAPCCI are *preliminary*.

^d For fabric filters and mechanical collectors, each quarterly value shown is the average of the Producer Price Indexes (PPIs) for the three months in question, *divided* by the average of the PPIs for January, February, and March 1994 (i.e., first quarter 1994).

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The Haztimator Knowledge-Based (Expert) System: Providing Design and Time/Cost Estimates for Hazardous Waste Remediation

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Development, implementation and tentative validation of a prototype of the Haztimator system, a knowledge-based (expert) system (KBS) intended to provide design and time/cost estimates for hazardous waste remediation projects, is presented. The prototype evaluates one potential remedial alternative, soil vapor extraction followed by vapor-phase granular activated carbon for air emissions control. Haztimator represents the first known expert system in the environmental field with a primary knowledge domain of system design. As shown by this work, the environmental field is a prime example of a problem domain where KBS development can be used as a tool for obtaining and exploiting "compiled" knowledge—knowledge which can be used to explain heuristics in terms of first principles.

INTRODUCTION

While many knowledge-based (expert) systems* (KBS) have been developed over the past decade, there has been a relatively slow emergence of KBS in the environmental field, a phenomena attributed to the following [1]:

- *Lack of Adequate Understanding:* The science for understanding/dealing with environmental problems is not well developed, and there are few consensus methods. This can be contrasted with the field of medicine (the problem domain in which KBS were first successfully applied) where a medical textbook is considered a Bible that even recognized experts will follow exactly.
- *Multi-Disciplinary Approach Required:* Few environmental problems can be solved by a single expert. A multi-disciplinary approach is often required to identify an optimal solution. However, incorporation of multiple expert knowledge into a KBS can be a significant problem, particularly when there is not universal consensus amongst the experts.

Despite such drawbacks, as of 1990, 69 KBS in the environmental domain had been identified [1]. Of these exist-

ing systems, only one directly involves engineering design—the Cost of Remedial Action (CORA) model, initially developed in 1987 by CH2M-Hill for the U.S. Environmental Protection Agency (USEPA). CORA is designed for use in developing and costing remedial actions for Superfund sites before or during the remedial investigation (RI) stage of the cleanup process, but prior to the feasibility study (FS) stage, when more detailed site-specific remedial alternatives are developed and associated cost estimates generated.

The CORA model is comprised of two independent, microcomputer-based systems [2, 3, 4]:

- *Knowledge-Based Consultation (Technology Selection) System:* Recommends optional remedial actions for a site based primarily on technical feasibility and USEPA policy, independent of cost considerations.
- *Database-Based Conceptual Cost Estimation System:* Develops site-specific cost estimates for the technologies required to implement the Consultation System's recommendations. This system contains a total of 40 individual cost modules, divided into the following five technologies series: Containment (5 modules), Removal (6 modules), Treatment (16 modules), Disposal (8 modules), Other (Misc.) (5 modules).

The CORA model served as the starting point for development of the Haztimator system described in this paper. Haztimator incorporates both the consultation (technology selection) and conceptual cost estimation system elements of the CORA model into a single KBS. Further, Haztimator specifically is designed to include the following features, each of which represent significant improvement over the CORA model:

- *Extensive human-computer interface* combined with "default" parameter values explicitly provided throughout, yielding a true KBS where users do not need a technical background to effectively utilize the system.
- *Predicted contaminant removal rate versus time curve along with an estimated time to clean-up.* In contrast, for specific application reasons, the CORA model is designed to estimate only first-year O&M costs—thus, removal rates and clean-up times are not calculated by CORA.
- *Automated design process* allows timely "what-if" scenarios to be performed to aid in the selection of the most

*KBS historically have been termed Expert Systems (ES); this practice remains prevalent today. However, KBS is a more accurate description of the systems referenced, and thus is used throughout this document.

plausible alternative as well as to evaluate the marginal value of additional information required to refine alternative designs.

- *AutoCAD component.* Haztimator includes an integral AutoCAD component which can provide a site-specific 3-D layout of the proposed system. Further, the design model and the AutoCAD layout are fully interactive, allowing for relocation or re-sizing of facility components with such changes being automatically reflected in revised system cost estimates.
- *"Transparent" solution approach,* providing detailed, unit cost-based break-downs of computed capital and O&M costs at both individual item (e.g., vent, piping, valves) and aggregate (e.g., extraction vent system) levels. From this breakdown, the user can easily identify major cost elements.
- *Improved cost estimation capability.* The cost estimates generated by CORA have an assigned accuracy range of +50 to -30 percent [2]. In contrast, by simulating the detailed design process, Haztimator is targeted to provide costs estimates in the accuracy range of ± 20 percent.

TARGETED PROBLEM DOMAIN

For the prototype version of Haztimator, the remedial alternative selected for primary focus consists of two technologies: soil vapor extraction** (SVE), followed by vapor-phase granular activated carbon adsorption (V-GAC). SVE technology is the current technology of choice for removing volatile organic compounds (VOC) from permeable vadose zone soils.

As such contamination is frequently found at hazardous waste sites as well as sites which have experienced gasoline or other hydrocarbon fuel spills, SVE has gained widespread use as a remedial technology. However, due to the technical complexities involved (emanating from: 1) dynamic, unsteady-steady operation, 2) real-world variability of the subsurface environment and 3) mass transfer limitations), SVE system design is strongly dependent on expert knowledge and site-specific constraints [5, 6]. Thus, the SVE design problem is well-suited to a KBS solution.

As SVE itself results in the contaminants being transferred from the soil to a vacuum-induced air stream, the contaminant-laden air needs to be purified prior to atmospheric release. V-GAC is the current technology of choice for cost-effective removal of the relatively low VOC mass loading frequently encountered in SVE operations.*** This conventional pollution control technology has been in widespread use for over 20 years, yielding a solid database of empirical performance data. Further, based on the available empirical data, a predictive semi-empirical model is available. Thus, design of V-GAC systems is relatively straightforward.

TECHNICAL MODELING

Development Approach

The principal focus of Haztimator is to provide cost estimates for hazardous waste remediation systems. In order to adequately perform this task, reasonably accurate technical modeling of the remediation system(s) under consideration is required. This is particularly true with regard to estimating the total time required for remediation. As such estimation is often a formidable task in real-world situations, a KBS approach was utilized to capture the expertise necessary for generating reasonable estimates. In capturing the required knowledge, a primary objective was to frame, to the maximum practical extent, such knowledge on a rigorous scientific basis (i.e., matching scientific theory with observational experience).

The overall result was selection of semi-empirical relations to perform the technical modeling, with necessary input parameter values heuristically-determined based on expert knowledge obtained from human experts as well as from literature reports. Guiding the selection were the following basic tenets set forth for the Haztimator system:

- *Simple, but not simplistic, modeling:* Based on the desire to frame observational experience within existing theory.
- *Able to handle a majority of cases,* which yielded two sub-tenets:
 1. *Flexible modeling*—Modeling knowledge must be flexible enough to capture a majority of potential cases. Such flexibility, however, typically comes at the cost of reduced model sophistication.
 2. *Not all cases handled*—Certain cases cannot be properly resolved by a KBS as they require in-depth analysis by a human expert. Such system limitations must be explicitly relayed to users when they attempt to analyze these atypical cases.
- *Chemical-specific design.* Under the CORA model, SVE design is based on "typical" contaminants. In contrast, Haztimator performs the design based on the specific contaminant(s) present. The compounds included in the prototype system are the seven VOCs that appear on the list of the most frequently identified contaminants of concern at Superfund NPL sites, namely:
 - BTEX (Benzene, Toluene, Ethyl-Benzene, and Xylene)
 - 1,1,1-Trichloroethane (TCA)
 - Tetrachloroethylene, also known as perchloroethylene (PCE)

Other compounds can be easily added to the Haztimator system—the property values required for modeling (Henry's constant, saturated vapor pressure, soil-water partition coefficient, liquid density and refractive index) are widely available for most common contaminants.

Technology Screening Module

As noted earlier, Haztimator is designed to incorporate a consultation (technology selection) element as well as a conceptual cost estimation system element into a single KBS. The consultation element is implemented via a technology screening module. Within this module, operational definitions for key parameters are incorporated. Based on user input and the key operational definitions, the appropriate technology (ies) are selected for further analysis.

** Alternatively referred to in the literature as: *in situ vapor extraction, in situ or soil venting, in situ or soil vapor stripping, in situ or soil vacuum extraction, in situ volatilization, and in situ aeration.*

*** *The modular nature of the Haztimator prototype permits future insertion of competing technologies such as catalytic oxidation. Further, for relatively high mass loading rates, the user is notified that V-GAC is not a cost-effective option; in such situations, the system does not generate a V-GAC design.*

For the prototype, the screening module focused on establishing the cost-effective area of application for the two technologies of concern, SVE and V-GAC. If a particular case falls outside that established area, the user is informed that SVE and/or V-GAC technology is not appropriate and offers a potential alternative(s) (in an expanded version of Haztimator, design and cost-estimation of a potential alternative(s) would be automatically performed).

With respect to SVE, it is the current technology of choice for removing VOC from permeable vadose zone soils. Therefore, operational definitions of what constitutes a VOC and a permeable soil were incorporated into the screening module as follows:

- **VOC:** Compounds having, at 20°C, a Henry's law constant and saturated vapor pressure in excess of 0.1 (dimensionless molar or mass concentration ratio) and 1 torr (i.e., 1 mm of mercury), respectively [3].
- **Permeable soils:** Sandy soils (typical intrinsic permeability of 1 to 100 darcies) and some silty soils (typical intrinsic permeability of 0.01 to 1 darcies).

With respect to V-GAC, it is the current technology of choice for removal of VOC under relatively low mass loading rates. For the screening module, ≤ 50 lb/day (≤ 23 kg/day) was established as the operational definition of a low VOC mass loading rate.

Model Summary

For SVE/V-GAC system design, the required engineering parameters and their associated significance are as follows:

- **Design Parameters:** Extracted Air Flow Rate: Affects vacuum pump and V-GAC unit sizing. Vent Design Radius (Effective Radius of Influence): Affects number of extraction vents required.
- **Performance Parameters:** Extracted Air Contaminant Concentration (Mass Removal) Versus Time Profile: Affects V-GAC capacity, usage rate and service life and determines required system operation time (i.e., remediation time).

The technical modeling ultimately adapted for the Haztimator prototype can be summarized as follows (see [7] for further details):

SVE:

- **Estimation of Extracted Air Flow Rate and Vent Design Radius:** Typically observed values were assigned based on the predominant soil type ("clayey sands, silts," "fine sands, silty sands," "medium sands," or "coarse sands, gravel"), modified, as necessary, based on existing surface conditions (e.g., presence of surface seals).
- **Estimation of Mass Removal Versus Time Profile:** Utilizing the general approach given in [8] and [9], separate analytical equations define the profile for cases where non-aqueous phase liquid (NAPL) is both present and absent. A third equation is used to determine the presence or absence of NAPL at a particular site, and, if initially present, at what point during the remediation NAPL will disappear. Non-equilibrium (i.e., mass transfer) effects are modeled via use of a single lumped parameter, η , the venting efficiency factor. Specific values for η were derived based on user characterization of the

relative homogeneity of the subsurface environment ("relatively homogeneous," "heterogeneous," or "highly heterogeneous").

V-GAC:

- **Estimation of V-GAC Capacity:** The form of the Dubinin/Radushkevich adsorption isotherm model equation presented in [10] is utilized for capacity estimation. Carbon-specific parameters incorporated into the prototype also are taken from [10] based on Calogon BPL carbon, a commonly utilized, commercially-available V-GAC.
- **Calculation of V-GAC Usage Rate and Service Life:** The usage rate is calculated using an equation derived from a simple mass balance; the service life is defined by an equation derived assuming a standard V-GAC contractor unit size of 1800 lb. (816 kg). Both parameters are dependent on the estimated V-GAC capacity. Since the capacity varies with the contaminant concentration in the incoming extracted soil vapor, and this concentration decreases with time, an iterative routine was developed to accurately determine the expected capacity and thus, frequency of V-GAC bed change-outs over time.

Several simplifying assumptions were made in development of the technical SVE/V-GAC model. One assumption, that of a uniform contaminant distribution existing at all times during the remediation, is considered particularly significant as it likely would be applied in modeling other remedial technologies for incorporation into an expanded Haztimator system. The uniform distribution assumption was deemed necessary based on Haztimator's intended use as a tool at the conceptual design stage, when detailed contaminant distribution data is not available (indeed, because of the substantial cost, time, and effort involved, such information may not be available even at the detailed design stage). While a uniform distribution is clearly not valid in field situations, it is felt that use of an average contaminant concentration will still yield reasonable performance predictions.

DEVELOPMENT/IMPLEMENTATION DETAILS

Computer Environment

The Haztimator prototype was implemented using Design ++, a high-level, object-oriented, shell-type system development tool. Design ++ is a design automation language built on Lisp. For Haztimator, Design ++ is interfaced to AutoCAD to display and manipulate geometric data. For purposes of the prototype, other basic data, such as cost data, are stored as objects within the system. However, Design ++ was selected partly because of its ability to interface with external data bases such as ORACLE. Thus, this ability could be taken advantage of in development of a beyond-prototype system.

Knowledge Acquisition

In developing the Haztimator prototype, access was gained to various experts from CH2M-Hill, Inc.; in addition, experts at various equipment suppliers were consulted. The one individual most directly involved in proto-

type development was Mr. James Hartley, who was identified as the "in-house" expert on SVE systems at CH2M-Hill. Hartley is a registered Professional Engineer who has extensive experience with SVE field installations. Discussions with Hartley indicated that his SVE design approach was truly observational-based, with limited formal quantitative modeling—typical characteristics noted for experts [11].

An initial face-to-face meeting with Hartley covered a wide range of basic issues, including:

- Initial problem definition required from users.
- Technology screening criteria.
- Engineering information required.
- Design philosophy.
- Design details/specifications.
- Practical system configuration/layout.

From this initial meeting, a summary document was drafted. This document served as the baseline guidance for prototype development; subsequent modifications were performed as required during the course of actual prototype development and implementation.

During subsequent on-site visits for additional knowledge acquisition purposes, the Haztimator prototype was demonstrated to Hartley. From his feedback, which encompassed a wide range spanning from technical points to user interface to possible system extensions, appropriate modifications were made to the prototype. These demonstrations also aided in maintaining Hartley's enthusiasm for and understanding of the KBS as it was being developed.

Input/Internal Processing/Output

Input. Figure 1 represents a simplified soil cross-section and associated contamination contours for a hypothetical site that Haztimator can be applied to for generation of a remedial design, whether involving SVE/V-GAC or other alternatives. The basic input required is designed to be fairly minimal and consists of:

- Predominant soil type (coarse sand/gravel, medium sand, fine/silty sand, or clayey sand/silt) of distinct soil layers.
- (Average) Depth and thickness of distinct soil layers.
- Predominant contaminant detected in each soil layer, and the extent of contamination (i.e., physical dimensions).
- Contaminant concentrations derived from concentration contour information (if available) or estimated average concentration.
- Pilot study information (if no such information is available, the system will use established default values based on predominant soil type).

Internal Processing. Generation of the design solution is governed by the product structure which defines legal solutions. Haztimator first performs an initial screening of alternative remedial actions (for example, treatment of site soils) and determines the set of potential technologies which can be used to accomplish the selected remedial action (for example, SVE). Haztimator includes these technologies as alternatives in the product model.

In the second stage, the design parameters associated with each technology are calculated to obtain physical designs, capital and operating costs, and clean-up time estimates for each alternative. The system then selects the most cost-effective alternative and generates a 3-D system layout through AutoCAD.

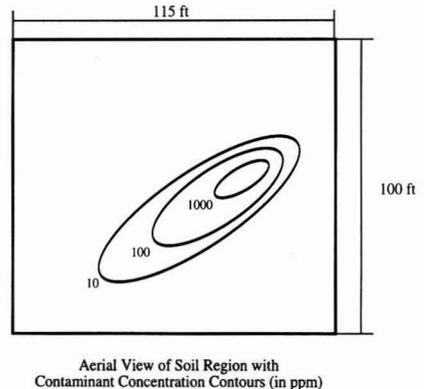
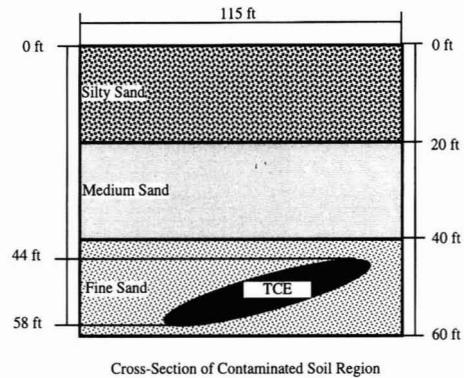


FIGURE 1 Haztimator input: contaminated soil cross-section and contamination contours.

Output. Output from the Haztimator system consists of four components:

- Product (design) model.
- AutoCAD model of the remedial system layout (see Figure 2 for an example of the AutoCAD output for a SVE/V-GAC system).
- Cost estimate reflecting capital and O&M costs at both individual item (e.g., vent, piping, valves) and aggregate (e.g., extraction vent system) levels.
- Clean-up time estimate and estimated contaminant removal rate versus time curve.

The interactive nature of the design model and the AutoCAD layout permit the designer a level of autonomy over design decisions. Facility components can be relocated or re-sized at the discretion of the designer, and such changes can automatically be reflected in a revised cost estimate.

VALIDATION

The validation effort conducted focused on the technical modeling aspects of the prototype. Both internal- and external-type validation work were performed.

Internal Validation

The Haztimator prototype was demonstrated periodically to others to provide the key form of internal validation for ensuring that the knowledge base and reasoning

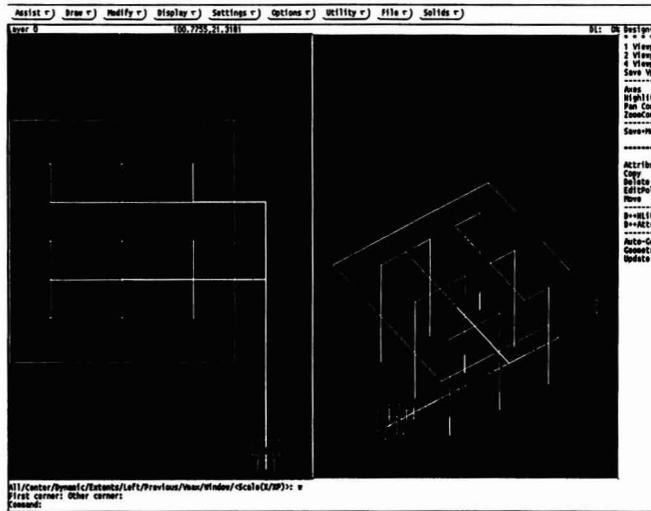


FIGURE 2 Example Haztimator AutoCAD output.

process accurately reflected the knowledge acquired. In particular, during on-site visits by the principal outside expert (Hartley), the Haztimator prototype was demonstrated to obtain his direct feedback. From this feedback, appropriate modifications were made to the prototype.

External Validation

External validation of a KBS can be a difficult and demanding task. While it was desirable to validate the Haztimator prototype to the maximum extent possible, the availability of "real-world" data hindered such efforts.[†] Thus, the external validation performed as detailed below is characterized as limited in extent, and the conclusions considered tentative in nature.

The external validation of the technical model conducted focused on two major SVE system engineering parameters, extracted air flow rate and contaminant mass removal versus time profile (the latter parameter quantified by the venting efficiency factor). For these parameters, a relatively straightforward validation could be performed. The general approach employed involved taking a given SVE system design as outlined in a case study, using the procedures built into Haztimator to predict SVE system performance, and comparing the Haztimator predictions to actual values.

The validation results for each of the two sites considered are summarized as follows (see [7] for details):

Groveland Wells Superfund Site (seven overlapping vents utilized for removal of TCE) [12, 13]:

Air Flow Rate: Field values were in reasonable agreement (within 25% on average) with assumed Haztimator default values for six of the seven vents evaluated. For

the seventh vent, similar agreement would be seen if the soil were re-classified as a fine sand rather than the coarse sand cited by the original investigators.

- **Venting Efficiency Factor:** Field-calculated values for all seven vents were within Haztimator default values cited for "typical" heterogeneous soil or relatively homogeneous soil.

New Jersey Industrial Site (single vent utilized for removal of TCA) [14]:

- **Air Flow Rate:** The flow rate achieved in the field was within 15% of the assumed Haztimator default value.
- **Venting Efficiency Factor:** The field-calculated value was in good agreement with assumed Haztimator default values cited for a highly heterogeneous soil, but significantly lower than that cited for a "typical" heterogeneous soil. A possible explanation for the relatively low efficiency value was found by noting that the initial contamination level was relatively low ($\ll 100$ mg/kg) while a relatively high removal was achieved (approximately 98% reduction in TCA contaminant concentration in the extracted soil vapor). Recent experimental work [15, 16] has suggested that the venting efficiency factor significantly decreases under such a combination of conditions. The default values incorporated into the Haztimator prototype are appropriate for less extreme conditions.

SUMMARY

The overall purpose of the research conducted was to evaluate the feasibility of employing a KBS approach to generate, based on limited information, engineering designs and corresponding time and cost estimates for hazardous waste remediation projects. Successful implementation and tentative validation of the Haztimator prototype, as previously detailed, has established that the KBS approach is feasible as well as effective. This success was anticipated, as the characteristics of the design problem considered in the prototype (i.e., SVE/V-GAC) matched

[†]SVE is a patented technology, and there exists vendors whose primary business involves field installation and operation of SVE systems. This situation, coupled with the current reliance on expert knowledge for SVE system design, has resulted in only limited data entering the public domain.

those of problem domains where KBS solution approaches have been successfully utilized.

Haztimator represents the first known KBS in the environmental field with a primary knowledge domain of system design. The potential implications to the project management process offered by the system are elucidated elsewhere [17].

CONCLUSIONS

It is believed that this work effort effectively demonstrates the potential value of a KBS solution approach in the problem domain of environmental remediation. Due to the complex process interactions involved and inherent variability of natural systems, it is unlikely that theory alone can be applied a priori to design/performance modeling of "real-world" systems. Further, from KBS system development efforts, existing heuristics can be evaluated and/or reconciled with existing theory to the benefit of both academics and practitioners. The ultimate value of a KBS approach lies in capturing/developing "compiled" knowledge—that knowledge which can be used to explain heuristics in terms of first principles. The value of compiled knowledge lies in its potential for being successfully applied beyond the limits of formal theory. As shown with the Haztimator prototype, the environmental field is a prime example of a problem domain where KBS development can be used as a tool for obtaining and exploiting such compiled knowledge.

ACKNOWLEDGMENTS

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LITERATURE CITED

1. **Hushon, J. M.**, "Overview of Environmental Expert Systems," in "Expert Systems for Environmental Applications," J. M. Hushon, editor, American Chemical Society, New York, pp. 1-24 (1990).
2. **Biggs, R. K., K. Klink, and J. Crenca**, "The Cost of Remedial Actions (CORA) Model: Overview and Applications," Proceedings of HAZMACON 89, Santa Clara, CA (1989).
3. **CH2M-Hill**, "Cost of Remedial Action Model Users Manual (Version 3.0)," 338 pp. (1990).
4. **Chenu, M. T., and J. A. Crenca**, "The Cost of Remedial Action Model," in "Expert Systems for Environmental Applications," J. M. Hushon, editor, American Chemical Society, New York, pp. 162-175 (1990).
5. **Cho, J. S., and D. C. DiGiulio**, "Pneumatic Pumping Test for Soil Vacuum Extraction," *Environmental Progress*, **11**(3), pp. 228-233 (1992).
6. **Nyter, E. K., R. W. Macneal and D. C. Schafer**, "VES Design: Using Simple or Sophisticated Design Methods," *Ground Water Monitoring Review*, Summer 1994, pp. 101-104 (1994).
7. **Staudinger, J.**, "The Haztimator Prototype: A Knowledge-Based (Expert) System Proving Design and Cost Estimation of Hazardous Waste Remediation Projects," Engineer Thesis, Stanford University, 124 pp. (1994).
8. **Johnson, P. C., M. W. Kembrowski, and J. D. Colthart**, "Quantitative Analysis for the Cleanup of Hydrocarbon-Contaminated Soils by In-Situ Soil Venting," *Ground Water*, **23**(3), pp. 413-429 (1990).
9. **Roy, W. R., and R. A. Griffin**, "An Analytical Model for In Situ Extraction of Organic Vapors," *Journal Hazardous Materials*, **26**, pp. 301-317 (1991).
10. **Crittenden, J. C., R. D. Cortright, B. Rick, S. Tang, and D. Perram**, "Using GAC to Remove VOCs from Stripper Off-Gas," *Journal of the American Water Works Association*, **80**(5), pp. 73-84 (1988).
11. **Waterman, D. A.**, "A Guide to Expert Systems," Addison-Wesley, Reading, MA, 419 pp. (1986).
12. **U.S. Environmental Protection Agency**, "Technology Evaluation Report: SITE Program Demonstration Test—Terra Vac In Situ Vacuum Extraction System—Groveland, Massachusetts—Volume I," U.S. EPA, Risk Reduction Evaluation Laboratory, Cincinnati, OH, EPA/540/5-89-003a, 97 pp. (1989).
13. **U.S. Environmental Protection Agency**, "Terra Vac In Situ Vacuum Extraction System: Applications Analysis Report," U.S. EPA, Risk Reduction Evaluation Laboratory, Cincinnati, OH, EPA/540/A5-89-003, 52 pp. (1989).
14. **Clarke, A. N., R. D. Mutch, P. D. Mutch, and D. J. Wilson**, "In Situ Vapor Stripping: Results of a Year-Long Pilot Study," *Hazardous Materials Control*, **3**(6), pp. 25-39 (1990).
15. **Farrell, J., and M. Reinhard**, "Desorption of Halogenated Organics from Model Solids, Sediments, and Soil under Unsaturated Conditions. 2. Kinetics," *Environmental Science and Technology*, **28**(1), pp. 63-72 (1994).
17. **Oralkan, G. A., J. Staudinger, R. E. Levitt, and P. V. Roberts**, "The Haztimator—Knowledge-Based Time and Cost Estimating of Hazardous Waste Remediation Projects," Working Paper #23, Center for Integrated Facility Engineering, Stanford University, 20 pp. (1994).

Pb Mobility and Extractant Optimization for Contaminated Soils

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Alternative technologies for the remediation for inorganic lead contaminated soils must be evaluated in addition to conventional standard technologies, such as stabilization, to help ensure the best technology was selected for implementation of the remediation solution. Innovative technologies such as extractive soil washing may provide an economical alternative to reaching remediation cleanup goals while, at the same time, protecting human health and the environment.

Extraction of inorganic Pb from contaminated soils has been previously demonstrated using strong acids or chelating reagents. For example, aqueous solutions of chelating agents such as citric acid, diethylenetriaminepentaacetic acid (DPTA), sodium ethylenediaminetetraacetate (EDTA), sodium nitrilotriacetate (NTA) have been used to desorb metals from soils [1, 2]. Also investigated were strong acids, having concentrations up to 2 N, for extraction of metals from sandy soils [3]. Commercial pilot scale systems have been reported to utilize HCl at an extraction pH range of 1.8–2.2 to recover lead from contaminated soils [4]. Chloride complexation of lead can greatly enhance the solubility of lead in solution [5, 6]. Lead also will complex in solution with acetic or citric acid [7].

Incorporating acids or chelating agents with soil washing technologies may extract inorganic Pb species from contaminated soils. However, the feasibility of aqueous based extraction of organic lead species such as tetraethyl lead, and its related byproducts produced by weathering, was unknown. Weathered, contaminated soil core samples were obtained, composited and homogenized in 5 gallon HDPE buckets, and the homogenized sample was characterized. The soils were contaminated predominantly with inorganic Pb as well as trace quantities of organic Pb species. Therefore, a research program was carried out to investigate the feasibility of in-situ or ex-situ extractive soil washing to recover inorganic and organic lead contaminants from soil. Literature approaches utilizing acids, chelating agents, or combinations of these, were tested for extraction efficiency. Additional goals included optimizing lead extraction while minimizing extractant chemistry strength to ensure safety and to minimize cost. Both in-situ and ex-situ extraction techniques were simulated at bench scale, and the effects of these methodologies on organic lead species were also investigated.

SOIL CHARACTERIZATION

Contaminated soil samples were visually distinct from one another. One sample appeared as a dark, organic rich silty soil with sand lenses (Sample A), and the other was a sandy soil mixed with clay lenses (Sample B). The soil samples were homogenized via a coning and quartering sifting method. The mixed soil material that passed the 1/4" mesh was reserved for the laboratory studies detailed in this report. The samples were analyzed for total lead and organic lead (xylene extractable) species. Even upon thorough homogenization of the samples, inherent variability was still observed within the same sample. The total lead results were varied due to the heterogeneity of the soils; therefore, the data (Table 1) are presented as an average \pm a standard deviation. The samples ranged from neutral to mildly alkaline in nature. Sample A was slightly more alkaline and also exhibited the highest total lead content and organic lead content. The organic lead content was below 0.1% of the total lead content for all of the samples.

LEAD MOBILITY

Toxicity Characteristic Leaching Procedure

The TCLP (Toxicity Characteristic Leaching Procedure) is an extraction procedure that utilizes a buffered or a mild aqueous acetic acid solution at a solid to liquid ratio of 1:20 [8]. The resultant extract is then analyzed for components of concern. If the levels exceed the EPA limit, the solid material is then to be regulated as a hazardous waste with a characteristic waste code classification. The TCLP test was carried out on the two samples of focus in this investigation. The extracts for Sample A and Sample B were well above the EPA limit for lead of 5.0 mg/L, refer to Table 1.

TABLE 1. Soil Characterization

	Sample A	Sample B
Soil description	silty soil	sandy soil
Soil pH	8.10	7.76
Total Pb (mg/kg)	6692 \pm 1305	1611 \pm 177
Organic Pb (mg/kg)	43.4	7.5
TCLP Pb (mg/L)	28.65 \pm 8.98	42.75 \pm 1.06

Approximately 8.6% of the total lead in the black sludge was available for leaching via TCLP, and 53% of the total lead in the sandy material had leached into solution during the TCLP analysis.

TCLP is a regulatory test and does not simulate the total amount of contaminant available for leaching in the sub-surface environment. There are several other tests available to simulate either acid rain precipitation and/or mobility in the groundwater. One of these tests, the Static pH Leaching Test, was chosen to evaluate the lead mobility of the samples.

Static pH Leaching Test

The Static pH Leaching Test was carried out (in duplicate) on the samples to observe the leaching of contaminants under more exhaustive aqueous conditions, without acetate complexation, in order to better simulate rainwater/groundwater mobility. The Static Leaching Test is a standard leaching test developed in The Netherlands for quantification of the maximum amount of contaminant available for leaching from combustion residues [9]. This test employs a neutral to mildly acidic aqueous extraction, and is carried out at a 1 gram to 100 ml solid to liquid ratio to avoid solubility limitations. The first step of the leaching test was carried out by agitating a soil slurry (8 grams soil and 800 mls water) for 4 hours and by controlling the pH at 7. The slurry was then filtered, and both the solid and extract saved. The soil was subsequently re-extracted for another 4 hours and controlled at a pH of 4 (once again at a 1 g solid to 100 ml water ratio). The acid/base solutions used to adjust the pH to the desired setpoint (of either pH 7.0 or 4.0) were 0.1 N NaOH and 0.1N HNO₃. The slurry was then filtered, and the extract combined with the solution from the first step. The combined extract was then analyzed for anionic and metallic species (Table 2). The data are represented as an average \pm sample standard deviation.

Elevated levels of anionic species such as chloride and sulfate were dissolved into solution. Several metals were also leached from the samples. The maximum amount of lead available for leaching (as determined by the Static pH Leaching test) was 416 and 260 mg/kg for Samples A and B, respectively. The percentage of readily leachable lead

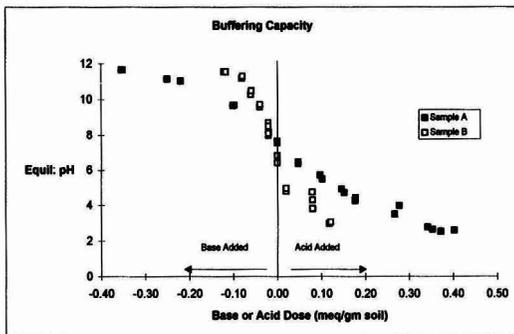


FIGURE 1 Soil buffering capacity.

was 6.2% for Sample A and 16.1% for the Sample B. The TCLP test predicted a similar amount of leachable lead available from Sample A (approximately 8.6%). However, the Static pH Leaching Test predicted a lower amount of Pb available from Sample B versus the TCLP test (16.1% versus 53%) as the TCLP extraction uses dilute acetic acid solutions. The amount of available lead for leaching is increased due to acetate complexation of Pb.

Soil Buffering Capacity and Lead Leachability Dependence on pH

Batch extractions were carried out on both samples to estimate the buffering capacity of the soils and to observe the total lead leachability dependence on pH. Samples were agitated with dilute aqueous solutions of HNO₃ or NaOH for 24 hours at room temperature. To observe the leaching dependence of pH, these acid and base solutions were chosen so that no ligands to complex with Pb would be added to the system (Figure 1). Extraction with deionized water alone indicates a dose of 0.00 milli-equivalent per gram of soil (meq/g). Increasingly alkaline solutions are represented by negative meq/g and increasing pH, while incremental acid additions are depicted by positive meq/g and a decreasing pH. Sample A had a significantly higher buffering capacity than Sample B.

The resultant extract was then analyzed for pH, Pb, and other assorted metals and anions. Results for Pb mobility

TABLE 2. Static pH Leaching Test Results

Species	Sample A (mg/L)	Sample B (mg/L)	Sample A (mg/kg)	Sample B (mg/kg)
F ⁻	1.60 \pm 1.00	0.64 \pm 0.19	309 \pm 189	124 \pm 42
Cl ⁻	14.1 \pm 0.7	8.8 \pm 0.4	2740 \pm 98	1707 \pm 131
N/NO ₃ ⁻	9.7 \pm 0.3	2.9 \pm 0.1	1885 \pm 28	566 \pm 48
SO ₄ ⁻	140.0 \pm 114.6	30.5 \pm 7.9	27048 \pm 21892	5963 \pm 1746
Ca	59 \pm 48	10.4 \pm 2.3	11403 \pm 9183	2035 \pm 515
Fe	0.07 \pm 0.03	0.14 \pm 0.0	13 \pm 5	28 \pm 0
Mg	1.4 \pm 0.3	0.64 \pm 0.08	272 \pm 51	125 \pm 21
Mn	0.16 \pm 0.05	0.06 \pm 0.01	30 \pm 9	12 \pm 2
Na	23 \pm 4	9.1 \pm 1	4369 \pm 624	1764 \pm 50
Pb	2.15 \pm 0.54	1.34 \pm 0.02	416 \pm 100	260 \pm 5
Si	0.77 \pm 0.18	0.29 \pm 0.01	148 \pm 32	56 \pm 1
Zn	0.07 \pm 0.03	0.07 \pm 0.01	13 \pm 6	13 \pm 2

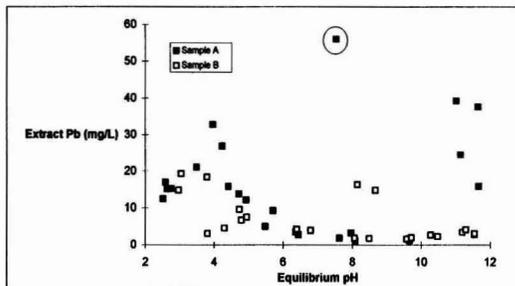


FIGURE 2 Lead leachability dependence on pH.

dependence on pH are presented in Figure 2. The samples' lead leachability was dependant on pH due to the amphoteric nature of lead. Pb was most leachable below a pH of 3 or 4 and above a pH of 11 for Sample A. Lead mobility was increased below an equilibrium pH of 3 or less for Sample B. Higher Pb leachability was observed for an extract sample of Sample A at an equilibrium pH of 7 to 8 (data point circled). It was not possible to replicate this, and the data point was considered as an outlier. Differences in lead mobility at similar pH values were observed during this evaluation, indicating the need to consider the solid material's inherent heterogeneity upon conducting leaching studies and data evaluation.

Sample B exhibited higher amounts of leachable Pb via TCLP (Table 1). The extracts of Sample B were further analyzed for anions and metals to generally characterize the leaching behavior of other constituents within the soil sample and to observe their effect on Pb leaching. The chloride concentration removed from the soil was approximately 1300 mg/kg soil throughout the equilibrium pH range. The leachable sulfate was more variable and ranged from 5000 mg/kg soil in the alkaline region to 9000 mg/kg soil at more acidic conditions. Calcium was steadily released upon increase in solution acidity, while Fe was mobile only at an acidic pH. The amphoteric leaching behavior of Si was similar to that of Pb. Fe and Al were leached from the soil under acidic conditions in a manner similar to that of Pb. Pb bound to the aluminosilicate clay matrix was being mobilized as the more acidic solutions attack the soil matrix and released increased amounts of Si and Al. The simultaneous release of Pb and Fe might be attributed to dissolution of crystalline and amorphous iron bound lead species.

EXTRACTANT EVALUATION

Extractant Evaluation and Equilibrium Batch Extractions

Several batch extractions were carried out for 24 hours on 1 g soil samples in 10 ml of solution. Solutions were prepared utilizing several complexation agents. Since the fully alkylated organic lead species are fully soluble in ethanol [10], it was also investigated as a co-solvent to extract any organic lead species present. Hydrochloric, acetic, or citric acid were utilized as the acid source to achieve the optimum equilibrium pH. The previously described soil buffering capacity experimentation had determined that

lead mobility increased below a pH of 3 for Sample B. The acids of interest also provided complexing agents to increase lead solubility and enhance Pb extraction. For example, the solubility of lead in solution can be increased through chloride complexation [5, 6]. The cumulative formation constants for lead chloride complexation are listed below [11]:



Lead also will complex in solution with the addition of acetic acid and citric acid [7]. The cumulative formation constants for lead acetate complexation are listed below [11]:



NaOH was utilized to prepare caustic solutions. NaCl was added to the solutions as an additional source of chloride ions. All of the extractants were prepared initially as dilute aqueous solutions: ethanol was incorporated into the mixture subsequently. Most of the extractant solutions were tested on both samples. The results for Sample B are presented in Table 3. The extractant compositions were designed to maximize lead recovery while minimizing reagent consumption. Therefore the solution concentrations tested above were based on the samples' soil buffering. For example, a 0.012 N HCl was utilized in conjunction with the NaCl. The sodium chloride provided the additional chloride ion for complexation. Maximum lead recovery occurred with the aqueous acidic solutions and ranged from 70 to 89% Pb recovered. Approximately 20 to 30% of the Pb was mobile due to pH effects (around a pH of 3) solely as evident from the buffering capacity testing (Figure 2). This further illustrates the benefit of acid in conjunction with chloride or acetate complexation. The use of ethanol

TABLE 3. % Lead Recovered from Sample B (Total lead of sample B = 1611 mg / ks)

Extractant Solution Composition (aq.)	Final Extract pH	% Pb Recovered
NaOH/1.0N NaCl	8.7	1.0%
HCl/0.5N NaCl	2.86	86.8
HCl/1.0N NaCl	2.5	88.6
Acetic Acid	4.17	8.3
Acetic/1.0N NaCl	4.17	71.4
Citric/1.0N NaCl	3.42	79.9
70% of HCl/0.5N NaCl, 30% Ethanol	2.77	14.6
NaOH, 10% Ethanol	8.54	1.3%

as a cosolvent with the dilute HCl acid treatment interfered with the recovery of lead from the sandy soil, as evident in the decreased lead recovery.

Extractant D, the acetic acid solution, removed only 8% of the total Pb versus the TCLP leaching results, which removed approximately 53% of the total lead from Sample B. The extractant evaluations were carried out at a liquid to solid ratio of 10, while the TCLP is carried out at a liquid to solid ratio of 20. The TCLP test utilized an acetic acid concentration of 0.7 eq/kg while the acetic acid solutions listed above were much milder (0.08 and 0.12 versus 0.7 eq/kg). Additional acetic acid would be required for Extractant D in order to increase Pb recovery.

The residues from the hydrochloric and acetic acid treatments for Sample B were tested for TCLP leachability. The hydrochloric and acetic acid treatments reduced the TCLP extract Pb concentration to 2.56 and 2.17 mg/L, respectively. The untreated Sample B TCLP Pb was 42.75 mg/L.

Sequential Batch Experiments

Three sequential batch equilibrium extractions were carried out on the two solid materials using a dilute hydrochloric acid solution with 0.5 N NaCl. The acidity of the hydrochloric acid solution was previously determined in the buffering capacity curves (Figures 1 and 2) as the acidity dose required to achieve an equilibrium pH of 3 (optimum for lead dissolution). For example, a solution of 0.04N HCl was used for Sample A (silty soil) and 0.012N HCl was used for Sample B (sandy soil). Soil samples were agitated with an extractant solution for 20 to 24 hours at a liquid to solid ratio of 10 (ml/gm). The soil/water slurry was centrifuged to separate the aqueous phase, and the liquid decanted. The extraction process was then repeated. A fourth extraction was carried out on the residuals using deionized water to remove residual chloride from the soils as a post treatment process step.

The extracts were analyzed for pH and total Pb content. The data were then normalized over the total amount of lead removed from extraction rounds 1 through 4 for ease in comparison (refer to Figure 3). Lead was recovered most readily from the Sample B (sandy material), while lead was removed more slowly from the Sample A (silty soil). Sample A contained the highest amount of total lead present on the solid, as well as an increased buffering capacity. A secondary batch extraction may be necessary on the Sample A material to reduce the lead content depending on desired clean-up goals.

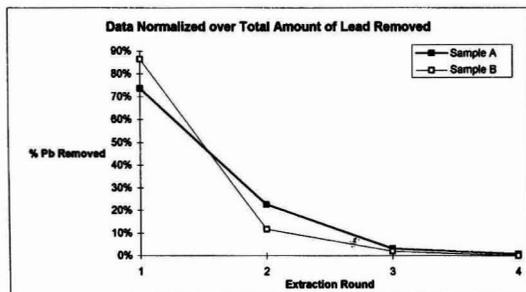


FIGURE 3 Sequential batch equilibrium extractions.

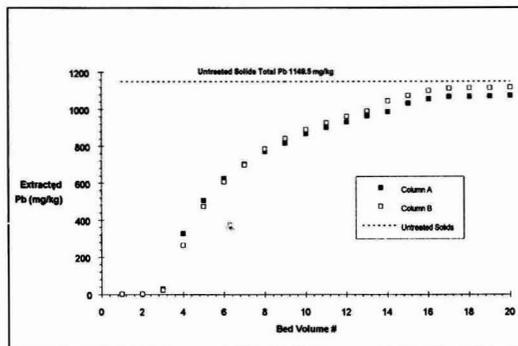


FIGURE 4 Column test: cumulative extracted pB.

Column Leaching Studies

Laboratory bench scale soil columns were utilized to assess the feasibility of *in situ* extraction of the contaminated soil. The Sample A material was mixed with work sand to increase its permeability. The sample was mixed at a ratio of 20% Sample A to 80% work sand to give a total Pb content of 1150 mg/kg. The columns were designed to hold a 20 ml bed volume of contaminated soil material (moist soil packing density 1.7 gm/ml). Two bed volumes of deionized water were allowed to percolate through the soil bed, followed by 14 bed volumes of dilute HCl/NaCl extractant (0.03N HCl/0.5N NaCl). Following extraction, the soil was rinsed with 2 sequential deionized water washes, neutralized with dilute caustic solution (0.03N NaOH), and rebuffered with a dilute buffer solution (0.1M K_2HPO_4). This was carried out to neutralize the soil back to the original soil pH of the region.

The extract pH was initially pH 6.6 and was steadily decreased within 5 bed volumes, where it was maintained between pH 1.5 to 2.0. After the rinse, neutralization and rebuffering stages, the extract pH rose again to a value of 4.9. Each bed volume of material was captured and analyzed for Pb content; the data is presented in Figure 4. Approximately 95% of the total Pb was cumulatively recovered from the soil.

Organic Lead Extraction: Tetraethyl Lead Conversion

The effect of the extractant composition of organic lead species such as tetraethyl lead was also investigated. Aqueous extractant solutions were prepared, spiked with a 1000 mg/l tetraethyl lead standard, and immediately analyzed via GC for tetraethyl lead (TEL) and triethyl lead chloride (TriEL). The samples were reanalyzed after 7 days, and then analyzed for total lead content for mass balance purposes. TEL rapidly disappeared for all of the samples within 7 days; TEL is nearly insoluble in water and therefore will precipitate out of solution and adsorb to the wall of the glass bottle. Tetraethyl lead is also readily broken down to the triethyllead radical in the presence of light [12], a reaction which also is catalyzed by silica or ferrous iron (Fe^{+2}). Any TEL conversion to TriEL would be indicated by the appearance of TriEL in the sample. TriEL was observed to be produced for the solutions containing dilute HCl or dilute HCl/NaCl, with the TriEL then being degraded at a slower rate. Other aqueous extractant solutions such as deionized water, acetic acid, acetic acid/NaCl, and

ethanol (control sample) were tested; TriEL production was not observed in any of these solutions. This appearance of triethyllead chloride in the HCl and HCl/NaCl solutions indicates that these inorganic lead extractant solution may have the potential to break down TEL to a more soluble form of TriEL, thus enabling extraction.

SUMMARY AND CONCLUSIONS

This study evaluated the feasibility of extractive soil washing to recover inorganic and organic lead contaminants from real weathered, contaminated soils. The focus of this study was to optimize lead extraction while minimizing extractant chemistry strength. However, the scope of this study did not include evaluation of treatment processes for lead removal and regeneration of the aqueous waste extract streams. Reagent evaluation and development for implementation of extractive soil washing processes should incorporate maximization of contaminant recovery and feasibility of reagent regeneration while considering economic factors such as wastewater treatment costs.

Contaminated soil samples were obtained and characterized for their chemical composition and evaluated for lead mobility. TCLP test results were compared to those of the Static pH Leaching Test. While both tests predicted a similar amount of leachable lead available from Sample A (approximately 8.6%), the Static pH Leaching Test predicted a lower amount of Pb available from Sample B versus the TCLP tests (16.1% versus 53%). The TCLP extraction incorporated acetate complexation of Pb to simulate co-disposal in a municipal waste landfill, while the Static pH Leaching test evaluated the maximum amount of lead available for leaching under more exhaustive aqueous conditions in order to better simulate rainwater/groundwater mobility. Buffering capacity experiments indicated the pH dependence to the total lead leachability. To fully assess contaminant mobility, one cannot rely on TCLP alone; additional extraction tests (batch and/or column) should be carried out.

Several extractant solutions were evaluated for total Pb removal. The more promising extractant solutions (for Sample B) were acetic acid or hydrochloric acid in an aqueous sodium chloride solution. These solutions recovered 75–85% of the total lead content in a single pass batch extraction, and reduced TCLP lead (for the sandy soil) by over an order of magnitude to below the EPA limit of 5.0 mg/L. Laboratory bench scale columns studies were used to probe the feasibility of *in situ* lead extraction. Site specific issues such as site geology and soil heterogeneity should be addressed prior to incorporation of in-situ extraction.

The effect of the hydrochloric acid/sodium chloride extraction solution composition on organic lead species such as tetraethyl lead was also evaluated. Tetraethyl lead conversion to soluble triethyllead chloride was observed to be enhanced by the presence of chloride in the aqueous hydrochloric acid/sodium chloride extractant solution.

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LITERATURE CITED

1. **O'Shaughnessy, J. C., R. C. D'Andrea, M. R. Canniff, S. St. Germain, S. Venkataramanappa, and M. J. Macaulay**, "Evaluation of In-Situ Soil Flushing Techniques for Heavy Metals Removal from Contaminated Soils," *48th Purdue Industrial Waste Conference Proceedings*, Lewis Publishers, Chelsea, Michigan, pp. 123–139 (1993).
2. **Peters, R. W., and G. Miller**, "Remediation of Heavy Metal Contaminated Soil Using Chelant Extraction: Feasibility Studies," *48th Purdue Industrial Waste Conference Proceedings*, Lewis Publishers, Chelsea, Michigan, pp. 141–167 (1993).
3. **Van Benschoten, J. E., B. E. Reed, R. R. Matsumoto, and P. J. McGarvey**, "Metal Removal by Soil Washing for an Iron Oxide Coated Sandy Soil," *Water Environment Research*, Vol. 66, No. 2, pp. 168–174 (March/April, 1994).
4. **Paff, S. W., and B. E. Bosilovich**, "Acid Extraction Treatment System (AETS) for Treatment of Metal Contaminated Soils," *20th Annual RREL Research Symposium Abstract Proceedings*, EPA/600/R-94/011, pp. 178–182 (March, 1994).
5. **Ontiveros, J. L.**, "Comparison of the Composition and Properties of Municipal Solid Waste Incinerator Ashes Based on Incinerator Configuration and Operation," Doctoral Dissertation in the Department of Chemical and Biochemical Engineering, Rutgers, the State University of New Jersey (May, 1988).
6. **Legiec, J. A.**, "Design and Scale-Up of a Heavy Metals Recovery Process from Municipal Solid Waste Incinerator Residues," Doctoral Dissertation in the Department of Chemical and Biochemical Engineering, Rutgers, the State University of New Jersey (May, 1991).
7. **Evans, L. J.**, "Chemistry of Metal Retention by Soils," *Environmental Science and Technology*, 23(9), pp. 1047–1056 (1989).
8. Federal Register, V55(61), March 29, pp. 11798–11877 (1990).
9. **Van der Sloot, H. A., O. Piepers, and A. Kok**, "A Standard Leaching Test for Combustion Residues," *Technical Report Bureau of Energy Research Project BEIP-21*, The Netherlands (1984).
10. **Mellan, S.**, *Compatibility and Solubility*, Noyes Development Corporation, Park Ridge, NJ, p. 251 (1968).
11. **Dean, J. A.**, *Lange's Handbook of Chemistry*, 14th Edition, McGraw-Hill, Inc., USA, pp. 8.83–8.103 (1992).
12. **Jarvie, A. W. P., R. N. Marshall, and H. R. Potter**, "Decomposition and Organolead Compounds in Aqueous Systems," *Environmental Research*, Vol. 25, pp. 241–249 (1981).

Simultaneous Hot Desulfurization and Improved Filtration in Coal Utilization Processes

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Much of America's vast coal reserves will remain unusable until technology capable of the effective, economic removal of particulate and sulfur emissions becomes more highly developed. Traditional calcium based sorbents, as well as more novel metal oxide sorbents, such as zinc ferrite and zinc titanate are effective in sulfur removal, but can be costly and do little to mitigate particulate within high temperature coal combustion and gasification streams. An innovative approach involving the use of classified, spent metal oxides appears to be a promising resolution to the particulate and sulfur dilemmas associated with most coal utilization processes. A number of such waste metal oxides have been tested, to assess their capacity for sulfur capture in sulfur laden oxidizing and reducing environments. Inert materials such as silica sand and traditional sorbents such as limestone and dolomite, were also evaluated to serve as reference data. Experimentation proved that the "once-through" spent metal oxide sorbents can effectively remove sulfur while simultaneously increasing the permeability of dust collected at downstream ceramic filter stations. Additionally, spent metal oxides are generated in large quantities as a result of metal processing, smelting, and refining operations, and are generally available at little or no charge, for use as cost effective sorbents in coal combustion and gasification processes. This paper suggests the use of such spent metal oxides in place of calcium based or regenerable pelletized metal oxide sorbents for the removal of sulfur dioxide (SO₂) and hydrogen sulfide (H₂S) from gas streams containing these components.

BACKGROUND INFORMATION

In recent years, ceramic filtration devices have shown that particulate removal levels well within the limits of New Source Performance Standards (NSPS), can be achieved at high process temperatures. Unfortunately, removal of the high levels of sulfur indigenous to much of our Nation's coal reserves has been problematic, requiring exotic (and expensive) sorbents, substantial coal feed pretreatment, or

a reduction in off-gas temperature to achieve acceptable sulfur emissions. Many researchers are aware that metal oxide sorbents can be used to effectively reduce sulfur emissions in such processes. However, because of the high cost of most metal oxides, especially such materials as zinc titanate and zinc ferrite, economic studies have shown that for such materials to be cost effective they must be used and regenerated as much as several hundred times before a return on investment is realized. Preliminary testing of such sorbents in a pelletized bed configuration, which lends itself to such a regenerative process, have shown that the strength of the pelletized metal sorbent significantly decreases in as few as five or six regenerative cycles. In view of this, it is apparent that a "once through," non-regenerable metal oxide sorbent can be a much more attractive solution from the standpoints of capacity, overall sulfur removal efficiency, and process economics. Moreover, in combination with ceramic filtration technology, the use of such an external sorbent becomes even more practical in that the sorbent can be introduced well upstream of the candle filter, have sufficient residence time for sulfur removal to take place, and then be easily collected on the surface of the ceramic filter, along with the ash and other particulate. By properly classifying and sizing the waste metal oxide sorbent particles, the permeability of the dust accumulating on the filter candles can be readily increased, resulting in lower pressure differentials, better pulse cleaning efficiency, and less susceptibility to candle pore "blinding."

The investigation into the utilization of spent metal oxides as sorbents was sponsored by U.S. Department of Energy research grants. Phase I test work consisted of the initial evaluation of which metal oxides functioned the best in oxidizing and reducing conditions. The most promising candidates from Phase I were then the focus of Phase II testing which is still in progress. The first half of Phase II test work consisted of TGA (Thermogravimetric) testing, chemical analysis, and packed bed testing. Ambient and high temperature testing of the metal oxides to assess their role as filter aids will be carried out in a filter unit at Industrial Filter & Pump Mfg. Co., Cicero, Illinois.

TABLE 1. Preliminary Test Series: Test Conditions

Test temperature:	Ambient
Test pressure:	3 psig
Sample size:	50 cm ³
SO ₂ or H ₂ S gas flowrate:	38 cm ³ /min
N ₃ Carrier gas flowrate:	82 cm ³ /min
Sample particle size:	75-106 micron; 90 micron average
pH endpoint:	5.00 (SO ₂); 6.5 (H ₂ S)

TESTING DESCRIPTION

Phase I

Preliminary tests involved the assessment of the sulfur affinity of waste metal oxides under controlled laboratory conditions by exposing a prepared bed of each material to sulfur dioxide (SO₂) and hydrogen sulfide (H₂S), in separate trials. The testing was performed at the Research & Development Department of Industrial Filter & Pump Mfg. Co., Inc. Table 1 lists the test conditions.

Iron oxide, zinc oxide, tin oxide, and a mixture of zinc/iron oxide were the metal oxides tested, these samples were obtained from Chicago area refineries and smelters. Although waste copper oxide was readily available and considered as another material suitable for testing, it was decided that since many waste copper oxide sources contain significant amounts of arsenic, no testing of this material would be undertaken for safety reasons. In addition to the testing of the above waste metal oxides, test trials were performed without any sorbents, with commercially available dolomite and limestone, and with inert or moderately inert sorbents, such as silica sand and diatomaceous earth, for reference purposes. In all of the above test scenarios, the flowrate of the SO₂ or H₂S gas and nitrogen carrier gas, which was used as a diluent to the SO₂ or H₂S, was held constant. Likewise, the sample volume and temperature for each test were maintained constant. The effluent gas was bubbled through analyzed collection water, and the elapsed time required to depress the pH of the collection water was recorded and indicated the end point of sulfur removal for each sample being tested.

By plotting the reduction in collection water pH as a function of time for each sample tested, a series of "break through" curves were generated and proved useful in directly comparing the sulfur affinity of each material. Initial "shakedown" trials involving nitrogen carrier gas and either SO₂ or H₂S, without a test sample bed, were conducted to determine the time delay (due to piping lengths and volumes) from the onset of the test until pH depression in the collection beaker. Both the effects on pH of the nitrogen carrier gas as well as the "time delay" associated with the internal volume of the test apparatus were used in the final data analysis. Test samples were dried in an air-circulated oven, after which the weight of the sample stabilized, indicating the removal of any moisture present. The samples then underwent particle size classification using a portable sieve shaker. Each sample material was classified and the particle fraction passing through a 140 mesh (106 micron opening) screen which was retained on a 200 mesh (75 micron opening) screen was utilized for each test specimen. This particle size is representative of that which

would be used to enhance filter cake porosity. Identical particle size fractions were used for each sample tested in the hope that the bed permeability in each sample trial would be essentially constant at constant gas flowrate conditions; also, the total available surface area exposed to the sulfur laden gas would be similar from one test to the next. Just prior to each test, the sample material was again dried in an air circulated oven to insure no moisture was retained, after which the classified sample was extracted and weighed for test purposes. Since H₂S is a weaker acid than SO₂ when dissolved in water, and because tap water (which was purposely selected in favor of distilled or demineralized water) was used in the collection beaker, the pH depression observed upon exhaustion of the sample bed in the H₂S test series would not be nearly as notable as that observed in the SO₂ test series. Due to the above observation, it was decided that a pH end point value of 6.50 would be used in the H₂S test series, and a 5.0 endpoint for SO₂. Additionally, total suspended solids (TSS) and total sulfites would be monitored and periodically recorded in the H₂S test series to serve as two other means of validating the data. The breakthrough curves are shown in Figure 1.

It can be shown from the graph that tin oxide exhibited the highest affinity for sulfur in SO₂ conditions, whereas zinc oxide and a mixture of iron oxide and zinc oxide had the higher sulfur affinity to H₂S conditions. Another aspect of Phase I research was to examine the availability, geographical location, and processes which generate the various metal oxides previously mentioned. Iron is the most widely used of all the metals, with approximately 85% of all the metal tonnage used for engineering applications in the United States based on iron. Tin is one of the earliest metals known to humankind commonly used as a protective coating or in alloying with other metals. Zinc is the fourth most widely used metal after iron, aluminum, and copper. More than 90% of the metal is used for galvanizing steel and for alloys. As of June 1996, the intrinsic value of the three base metal materials was as follows:

- Tin (composite) \$4.16/lb.
- Zinc (high grade) \$0.49/lb.
- Iron (steel) \$0.07/lb.

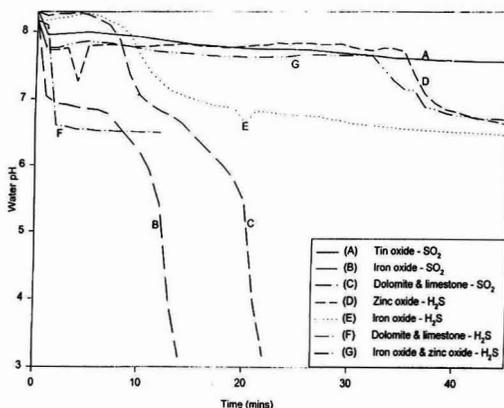


FIGURE 1 Preliminary test series breakthrough plots.

**TABLE 2. Sulfur Removal Capacity
(gm of "S" removed / kg of sorbent)**

Sorbent	Capacity in SO ₂ *	Capacity in H ₂ S*
Tin oxide	66.02	19.13
Iron oxide	21.22	59.86
Zinc oxide	14.92	70.22
Iron & zinc oxide	20.99	82.70
Dolomite & limestone	16.09	4.23

(*) 85% pure material.

These materials are inexpensive and easily obtained; in contrast, pelletized zinc ferrite or zinc titanate is significantly higher in cost. Even the most novel, fluidized zinc titanate formulations, such as "ZT-4," were reported to be \$7.91/lb, as of June, 1994. It should be emphasized that the intrinsic values shown above are commodity prices for the base metals of each material, and do not represent the cost of the corresponding waste metal oxides, which are much less. The sulfur removal capacity for each of these materials was calculated by using test conditions and values from the breakthrough curves, as shown in Table 2.

Phase II

Thermogravimetric (TGA) Testing

Tin oxide, zinc oxide, iron oxide, and a mixture of zinc oxide and iron oxide, were selected for TGA testing. This work was conducted by the Institute of Gas Technology in Des Plaines, Illinois. These sorbents were evaluated for reactivities with respect to H₂S and SO₂ using a high pressure, high temperature thermogravimetric analyzer (HPTGA) unit. The comparative sulfidation tests were conducted at 538°C (1000°F) using fuel gas containing 0.9% H₂S, 3.9% H₂ and the balance N₂; sulfation tests were conducted at 650°C (1200°F) using flue gas containing 1% SO₂, 3% O₂, and the balance N₂. During a typical TGA test, the sample weight, the rate of weight change, and the temperature of the furnace are recorded. The sample is contained in a platinum basket, suspended from a recording balance by a platinum wire chain, while a metered gas flow is introduced at the bottom of the reactor chamber. The desired composition of the reactant gas is obtained by mixing different streams of gases at pre-determined ratios. Any movement of the balance arm, because of a change in sample weight, is sensed by a linear differential transformer on the sample arm of the balance. A restoring force that is proportional to the change in weight is supplied to the opposite arm with an electromagnet. The recording balance control unit senses the force required to maintain a null and converts this into a signal proportional to the weight of the sample. The procedure for these tests included heating the sorbent in a nitrogen atmosphere to a pre-determined temperature. At this point the reactant gas mixture containing H₂S or SO₂ is allowed to flow past the sorbent while the change in sample weight is continuously monitored. The sample is exposed to the reactant gas until the sorbent is converted to its peak value. The weight gain-versus-time curve produced in these tests is used as a measure of reactivity and capacity of the sorbent tested.

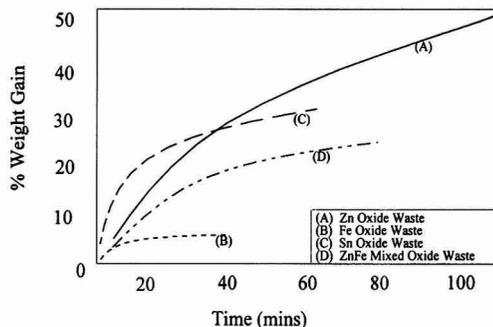
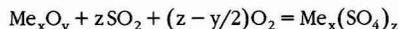


FIGURE 2 Comparison of sulfation kinetics at 650°C.

Results of TGA Tests: Sulfation Conditions

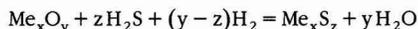
In the case of sulfation, the reaction may be represented by the following equation:



Initial sulfation tests at 870°C (1600°F) indicated no significant sulfation reaction with the zinc oxide waste at such a high temperature. This is consistent with the theoretical thermodynamic limitation of the metal oxide sorbents tested. Comparative sulfation tests were carried out at 650°C (1200°F). Since each mole of oxygen is replaced by 1 mole of sulfur and 4 moles of oxygen, the weight gains during the sulfation reaction are much more significant than during sulfidation. The results indicate that in terms of the overall sulfur capacity, zinc oxide waste is the best sorbent, followed by tin oxide waste and iron oxide as indicated by the graph of % wt. gain vs. time (see Figure 2).

Results of TGA Tests: Sulfidation Conditions

For a metal oxide Me_xO_y, the sulfidation reaction may be represented by the following equation:



The weight gain is therefore due to the exchange of sulfur (M.W. = 32 g/mole) and for oxygen (M.W. = 16 g/mole) during the sulfidation reaction. The results from comparative sulfidation tests at 538°C (1000°F) using all four metal oxide waste materials indicate that in terms of overall sulfur capacity, iron oxide waste is the best sorbent, followed by zinc oxide waste and tin oxide waste (see Figure 3). As in the sulfation tests, both the reaction kinetics and final weight gain of the ZnFe mixed oxide waste are intermediate between those obtained with each of the iron oxide waste and the zinc oxide waste, further indicating the consistency of the results.

TGA Testing II and Chemical Analysis

Next, the most promising candidate from each condition had to be chosen for more in depth testing. Based on results of earlier testing, iron oxide was chosen for sulfidation testing, and tin oxide was chosen for sulfation testing. Although zinc oxide possessed a higher capacity for sulfur capture, the tin oxide had a much higher reactivity which

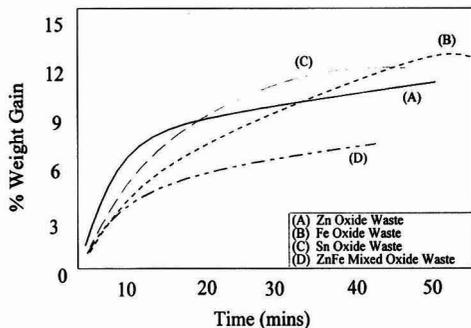


FIGURE 3 Comparison of sulfidation kinetics at 538°C.

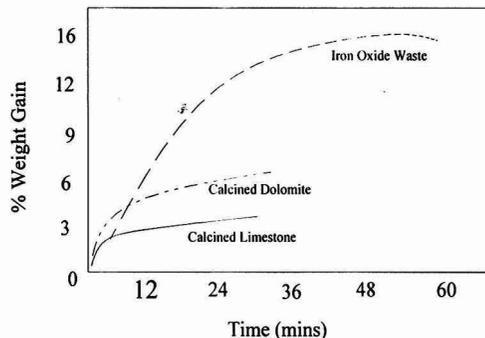


FIGURE 5 Comparison of sulfidation kinetics at 538°C.

is why it was selected. Monetary constraints prohibited testing of both.

Chemical analyses on the metal oxide waste samples were performed prior to TGA testing as follows: samples for metal analysis were prepared using acid digestions and/or sodium tetraborate fusion and were analyzed using an atomic emission spectrophotometer (ICP/AES). Samples for chloride analysis were analyzed by ion chromatography. Samples for sulfide sulfur and sulfate sulfur analyses were acid digested, and in the case of the sulfide analysis, a closed system was used where the evolved gases were collected in an alkaline peroxide sorbent. The resulting solutions were analyzed by ICP for sulfur.

The second phase consisted of sulfidation tests using the iron (Fe) oxide waste and sulfation tests using the tin (Sn) oxide waste. TGA tests were conducted to evaluate the effect of temperature on sulfidation and sulfation reaction rates of both waste materials. The sulfation reaction rate and sulfur absorption capacity of the Sn oxide waste were compared to those of limestone and dolomite at a temperature of 538°C. To make the comparisons meaningful, each of the limestone and dolomite samples was calcined at 850°C in flowing N₂ prior to sulfation and sulfidation tests. TGA testing was then carried out in the same manner as earlier described, except that the sulfated and sulfided samples underwent chemical analysis to determine the sulfur content afterwards. Figures 4 and 5 show the graphs comparing absorption capacities and reactivities of the two metal oxides in comparison to dolomite and limestone.

Clearly absorption capacity of Fe oxide greatly exceeds that of dolomite and limestone, whereas the capacity of Sn oxide falls intermediate between the two.

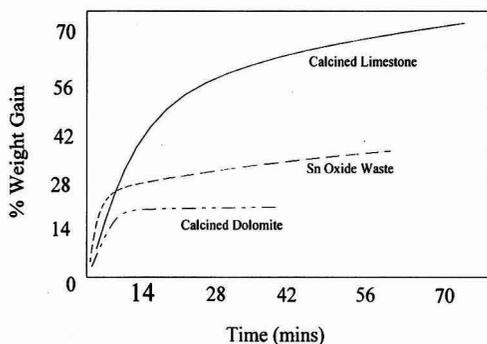
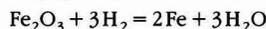
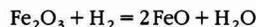
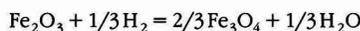


FIGURE 4 Comparison of sulfation kinetics at 650°C.

Chemical analysis performed subsequent to TGA testing uncovered some discrepancies between the recorded weight gain and wt. % sulfur analyzed. These results for the iron oxide sample are shown in Table 3.

A stability diagram was provided for the Fe-S-O system to help clarify the perplexing results. It was also explained that FeS₂ is more stable at lower temperatures and the portion of FeS₂ in the product mixture decreases with increasing temperature which may explain the higher weight gain at 450°C than at 538°C. At 650°C there are additional competing reactions, namely the reduction of Fe₂O₃ and sulfidation of the resulting products:



The results suggest that sulfidation at 650°C does not dominate reduction; in addition, reduction of Fe₂O₃ occurs to a much greater extent, possibly to the elemental Fe state, resulting in a total weight gain much lower than those achieved at 450° or 538°C. The relatively high rates of reaction above result in loss of oxygen and consequently loss of sample weight, leading to lower weight gain, or even weight loss when the reduction reaction dominates the sulfidation reaction.

At 450°C and 538°C, sulfidation dominates reduction of Fe₂O₃; when the maximum sorbent conversion in the sulfidation reaction is achieved, a slight weight loss is developed as the sample continues to be exposed to the sulfidation gas. This weight loss is due to the continued reduction

TABLE 3. Sulfur Content of Sulfided Iron (Fe) Oxide Waste Samples

Temp. (°C)	% Weight Gain (Experimental)	Weight % S (Chemical Analysis)
450	15.64	21.5
538	14.42	15.1*
650	5.90	28.2
650	6.41	31.1

*This number is expected to be about 25; the source of the discrepancy is not known at this time.

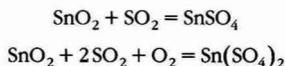
TABLE 4. Sulfur Content of Sulfated (Sn) Oxide Waste Samples

Temp. (°C)	% Weight Gain (Experimental)	Weight % S (Chemical Analysis)
550	23.11	8.68
650	34.39	6.74
750	26.91	6.40

of the iron oxide waste material. Reduction of the sample at the conclusion of sulfidation becomes more significant with increasing temperatures.

The sulfur analyses of reacted (sulfated) samples are presented in Table 4. These results indicate that although the tin oxide waste material exhibited a lower total weight gain during sulfation at 550°C than it did at 650°C or 750°C, the sulfur content of the sulfated sample was indeed highest at 550°C.

To help interpret these results, a stability diagram for the Sn-S-O system in the temperature range of interest to the experimental work was provided. Based on this figure, the product of sulfation is expected to be SnSO₄, Sn(SO₄)₂, or a mixture of the two tin sulfates, in accordance with reactions:



According to the stoichiometry of these reactions, a higher weight gain of a reacting sample should correspond to a higher sulfur content. However, the sample resulting from the sulfation test at 550°C possessed the highest sulfur content, despite showing the lowest weight gain at the conclusion of the sulfation test. This may be explained by taking into account the contribution to the sample weight gain of sodium. Although sodium accounts for about 10% of the tin oxide waste material, the molar concentration of sodium in the sample is very close to that of the tin, making the contribution of sodium very significant, especially at 550°C (compared to 650°C or 750°C).

TGA and Chemical Analysis Testing Conclusions

The results of the thermogravimetric analyses combined with chemical analyses of the sulfided materials indicate that iron oxide waste materials are very effective for removal of H₂S from the fuel gas in the temperature range of 450°C to 650°C. The results also indicate that 650°C offers the best operating point for desulfurization of fuel gases, using the iron oxide waste material as a once-through sorbent. Comparison of the reactivities as well as sulfur capacities of the iron oxide waste material with those of precalcined limestone and precalcined dolomite indicate that although the initial reactivities of precalcined limestone and precalcined dolomite are higher than that of the iron oxide waste, the effective sulfur capacity of the latter material is superior to those of the former materials, making iron oxide waste material a good candidate as a once through desulfurization sorbent.

The results of the TGA and chemical analyses of the sulfated tin (Sn) oxide waste material indicate that this material is very reactive toward SO₂ in the temperature range of 550°C to 750°C, and that the highest sulfur sorption capacity was achieved at 550°C. However, comparison of the reactivity and sulfur capacity of the tin oxide waste material with those of precalcined limestone and precalcined dolomite indicate that although the initial reactivity of the tin oxide waste material is slightly better than those of calcined limestone and calcined dolomite, its effective sulfur capacity is only about 50% that of precalcined limestone and about 60% that of precalcined dolomite. Therefore, this sorbent does not appear to be superior to limestone and dolomite for flue gas desulfurization.

CONCLUSION

Spent metal oxides can be utilized as effective and inexpensive sorbents to be used in place of traditional calcium based sorbents, or newer exotic and costly sorbents. These novel waste metal oxides remove sulfur from gas streams containing sulfur dioxide or hydrogen sulfide associated with coal utilization processes. Testing thus far has indicated that zinc oxide has the best sulfur removal capacity in the presence of SO₂, whereas iron oxide is best suited for H₂S environments. The use of selectively sized metal oxide particles to aid filtration by increasing the permeability of dust collected at downstream ceramic filter stations will be verified in future tests. It is expected that commercialization will follow test completion.

ACKNOWLEDGMENTS

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LITERATURE CITED

1. **Gangwall, S. K., and R. P. Gupta**, "Fluidized Bed Sorbents," (D.O.E. Contract No. DE-AC21-88MC25006) excerpted from the "Proceedings of the Coal-Fired Power Systems 94-Advances in IGCC and PFBC Review Meeting," Morgantown, WV DOE/METC-94/1008, Vol. 2, p. 646.
2. **Mohan, C. P., and J. T. Schrodt**, "Fuel Gas Desulfurization in Fluidized Beds of Gasifier Waste Ashes," American Institute of Chemical Engineers' Symposium, Ser. 211, Vol. 77 (1981).
3. **Robin, Allen**, "Integration and Testing of Hot Desulfurization and Entrained Flow Gasification for Power Generation Systems," U.S. D.O.E. Cooperative Agreement DE-FC21-87MC232277; from the "Proceedings of the Twelfth Annual Gasification and Gas Stream Clean-Up Systems Contractors Review Meeting," Morgantown, WV DOE/METC-92/6128, Vol. 1, p. 95.
4. **U.S. Dept. of Interior, Bur. of Mines**, Annual Reports for Tin, Zinc, Iron (1992).

Parametric Testing of Coal Electrostatic Precipitator Performance

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The effect of internal geometry, electrode type, and operating conditions on the performance of a coal electrostatic precipitator (ESP) has been analyzed by means of an extensive parametric testing program. Tests under different conditions of plate spacing, discharge electrodes, gas velocity, and energization wave form have been performed using two extreme coal types, with very high and low resistivity ashes, respectively. The study was made by means of a pilot installation operating with a flue gas slipstream drawn upstream of a power plant ESP. The experimental plant includes a specifically designed pilot ESP, able to admit an internal modification of plate spacing and electrode type. The ESP is equipped with a microprocessor controlled power supply which can generate both continuous and intermittent rectified current.

The measured sensitivity of the precipitation process to the dust properties, filter configuration, electrode type, and energization method is presented, covering both the ESP efficiency evolution and the associated power consumption. The results of this work allow to extract practical conclusions about specification of ESP design and size for a given application, and assess the conditions in which use of wide plate spacing, new electrode geometries, or intermittent current are actually advantageous.

INTRODUCTION

Although coal ESP technology is consolidated worldwide and a large amount of research and practical experience exists, most of this information is not available and, in some areas, more efforts are still needed to improve filter performance and power consumption, at least when high-resistivity ashes are involved. In these cases the units find serious difficulties in achieving the required efficiency and operation stability, and an important ESP oversizing is often used to reach the very high efficiency presently demanded to particulate control units.

Moreover, in recent years some new concepts have been introduced by ESP manufacturers trying to achieve the double objective of increasing ESP efficiency and, at the same time, to reduce both capital and operating costs. Among these new concepts, the most interesting are: wide plate spacing [1], new rigid electrodes [2, 3], intermittent energization [4, 5], and new electrical control systems [6], in addition to flue gas conditioning. Therefore, new units

tend to have a very different geometry, electrode design, and power supply than older ones. In addition, some insight has been made on rapping improvement and on advanced control systems. As a result, a better performance of ESPs is now expected, but some lack of knowledge remains, at least among ESP users, about the quantifiable real benefits of these changes and about their applicability to specific situations. In fact, the new ESP concepts have not always resulted in parametric optimization of the other related ESP components, and they are often promoted more taking into account their cost advantages than the actual improvement on ESP performance.

Under this perspective, the research project presented here, funded by OCIDE (Ministry of Industry - Spain) and Cía. Sevillana de Electricidad, has been performed with the main objective of studying ESP behavior when different coals and different filter configurations/energization methods are used. The primary aim of the project was to reach conclusions about the ESP design and sizing criteria which should be used as a function of the coal type.

METHODOLOGY

Experimental Facility

A pilot plant has been designed and built to accomplish the test requirements [7]. The plant is located at Los Barrios Power Plant (Cádiz, Spain), a 550 MWe coal-fired plant which consumes various types of international bituminous coals. The pilot installation is connected to a flue gas duct upstream of the power plant ESP and it includes a pilot ESP (PESP) and its auxiliary units and control systems. Figure 1 presents the plant layout where it should be noted that the plant also includes a bypassed spray drier desulfurization reactor.

The PESP main characteristics are presented in Table 1. The PESP design includes the following special features:

- All PESP internals (plate curtains, electrode frames, rapping hammers, etc.) are movable and it is possible to modify plate spacing, number of gas passages, electrode type, and electrode number fast and directly from the inside of the filter.
- The PESP energization system is capable of generating rectified continuous current or intermittent (pulsing) current, and even of combining both according to the electrical operating conditions of the filter.

Ash samples have been taken at PESP inlet and outlet sections, as well as from the hoppers, to evaluate particle size and other significant physical properties.

SELECTED PARAMETERS AND LEVELS

Types of Coal

Tests firing two different coals have been performed in order to analyze ESP behavior under very high-resistivity (coal A) and low-resistivity (coal B) conditions. The characteristics of both coals taken as median values from different batches are presented in Table 2. As can be seen, coal A is characterized by a medium ash content, a low sulfur content, and a very high ash resistivity; whereas coal B shows a lower ash content and lower resistivity. Although both coals have a similar sulfur content and produced ASTM class F ashes, substantial differences in fly ash resistivity should be related with the observed differences in coal ash composition.

Electrode Type

Three discharge electrode types have been used. The selection of these electrode geometries was aimed to assess the effect of electrodes belonging to three different general categories: E_1 = barb wire; E_2 = pipe-and-spike electrode; E_3 = twisted square rod.

Plate Spacing

Taking advantage of the versatility that the internal configuration of the precipitator allows (plate spacing can be

set at between 200 and 500 mm) three test spacings have been selected, corresponding to usual design specifications for commercial precipitators, to study its coupling effect with electrode type on ESP efficiency: A_1 = 300 mm (baseline); A_2 = 400 mm (wide plate space—European design); A_3 = 500 mm (very wide plate spacing).

Gas Flow Rate

In general, the velocity at which the gases flow through commercial ESPs is designed around an optimum estimated between 1 and 1.2 m/s. To evaluate the effect of this parameter on precipitation, tests were carried out for each of the following rates: V_1 = 0.8 m/s; V_2 = 1.1 m/s (baseline); V_3 = 1.4 m/s.

Number of Fields in Service

To study the evolution of the precipitation efficiency with a progressive increase in collection area, the performance in each case tested was evaluated establishing three levels for the active fields in service. In this way the differential efficiency of each of the fields can also be obtained: N_1 = Field 3, active; N_2 = Fields 2 and 3, active; N_3 = Fields 1, 2, and 3, active (baseline).

ESP Energization

Two types of voltage wave form have been used to determine the influence of ESP energization on performance and power consumption: W_1 = continuous rectified current (baseline); W_2 = intermittent (pulsing) rectified current.

Other Parameters

Other variables affecting precipitation were kept constant during tests to simplify the experiments and results processing:

- **Rapping frequency.** The influence of rapping frequency on the average efficiency is relatively low given the short duration and uniformity of the testing periods. The duration of the rapping and intervals between rapping were kept constant for all the tests, within typical values for commercial ESPs: a duration of 90 seconds at 5-min. intervals (1st field), 10 min. (2nd field), and 15 min. (3rd field).
- **Operating temperature.** All the tests were run with an adjustment for the gas temperature coinciding with the mean value registered at full load at the preheater outlet, at around 130–135°C.
- **Energization voltage.** The TRs microprocessor control system has the capacity for choosing automatically the voltage-current operation point, optimizing the energization of each electrical section according to the sparking level and average current. Consequently, for each of the tests carried out, the TR control unit was operated on automatic, so the voltage and current during tests in each field were among variables to be evaluated.

TEST PROGRAM

The test series indicated in Table 3 were performed in accord with the chosen parameters and levels. Each series

TABLE 2. Coal Characteristics

Property	Coal A	Coal B
Ultimate analysis (wt %, d.b.)		
• C	74.3	79.6
• H	4.1	5.1
• N	1.8	1.5
• S	0.7	0.8
• O	6.4	7.3
• Ash	12.7	5.7
Moisture (wt %)	8.0	11.3
HHV (kcal/kg, d.b.)	6800	7600
Ash composition (ASTM D-3682-78, wt %)		
• SiO ₂	39.6	61.3
• Al ₂ O ₃	33.1	18.1
• Fe ₂ O ₃	2.8	9.6
• CaO	8.5	2.5
• MgO	2.5	2.3
• Na ₂ O	0.4	1.3
• K ₂ O	0.8	2.4
• MnO ₂	0.06	0.06
• TiO ₂	2.1	0.9
• P ₂ O ₅	1.4	0.3
• SO ₃	6.1	0.7
Fly ash in-situ resistivity (Ohm · cm)	10 ¹² –10 ¹³	10 ⁸ –10 ⁹

TABLE 3. Test Series Matrix

Coal type	Coal A			Coal B		
	Barb	Pipe	T.Rod	Barb	Pipe	T.Rod
Electrode	300	X	X	X	X	X
Plate Spacing (mm)	400	X	X	X	X	
	500	X	X	X		

TABLE 4. Full Tests Included in Each Series

Test	Gas velocity (m/s)	Energization Voltage	Active Fields
1	0.8	Continuous	#3
2			#2 + #3
3			#1 + #2 + #3
4	1.1	Continuous	#3
5			#2 + #3
6			#1 + #2 + #3
7			Intermittent
8	1.4	Continuous	#3
9			#2 + #3
10			#1 + #2 + #3

corresponds to a combination of coal type, discharge electrode, and plate spacing. The test matrix for each series is presented in Table 4, where the settings for gas velocity, number of active fields, and energization mode used in the individual tests are indicated. Additional shorter tests (without dust sampling) using intermittent energization were performed in each series.

Before beginning the tests, the gas velocity distribution inside the precipitation chamber was adjusted and measured on a 48-point grid at different flow rates to assure the uniformity of velocity profile. Typical deviations were obtained in the velocity at around 18% of the mean value. This outcome is within the adequate range of operation for ESPs, calculated at levels of less than 25% of the average [11].

At the beginning of each series of tests corresponding to a type of coal, the opacimeter was calibrated, and particle extinction-concentration correlations were carried out to establish the correspondence between both magnitudes to continuously monitoring the levels of particle concentration in the exit gases.

Continuous operation tests were also carried out prior to the tests to find the response time to the operating variables and the ways boiler operation could possibly distort the tests in the pilot plant. Fluctuations in inlet particle concentration, moisture, and pressure were perceived to be produced by the preheater blowing and could affect the outcome of the tests. To avoid this interference, schedules were chosen for the tests that did not coincide with blowing periods.

DUST PROPERTIES

The most relevant difference between the tested fly ashes is their resistivity, as previously said very high for ashes of

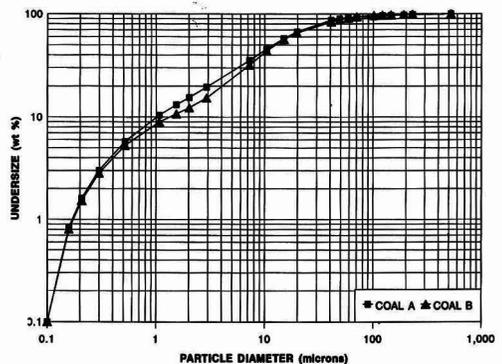
coal A and low for ashes of coal B. However, other interesting differences to be taken into account for test evaluation are the inlet concentration and particle size.

The input dust load of the different tests corresponding to coal A underwent variations in the 6,500 to 10,600 mg/Nm³ range, caused by boiler operation. This long-term variation in dust load was mainly due to unbalance between flue gas ducts promoted by some boiler settings. The boiler parameters with a greater incidence in the PESP inlet dust concentration were active mills, burners tilt, excess air, and load modulation. The representativeness of the tests in relation with the changes detected in the particle load was guaranteed after proving, by means of specific tests, that these changes had no significant effect on PESP efficiency. To do so, a series of samplings was carried out under constant operating conditions where the only variable parameter was the particle concentration at the PESP inlet, sweeping the entire range of tests. The efficiencies obtained were all of the same order, and provide dispersion levels similar to those obtained in series of samples carried out with the same input concentrations. The inlet particle concentrations corresponding to coal B (3,000 to 5,600 mg/Nm³) are significantly lower than those found for coal A because of its lower ash content. In relation with particle size, Laser-Coulter size measurements performed on ash samples isokinetically taken at the PESP inlet indicate that both fly ashes present a similar size distribution although ash from coal B is slightly coarser, as can be seen in Figure 2.

ELECTRODE CHARACTERISTICS

Different viewpoints exist regarding the desired attributes of a discharge electrode. One approach indicates that voltage should be maximized at the same time that uniformly distributed low current densities are maintained. On the other hand, the use of a proper current density (low for a high-resistivity dust and high for a low-resistivity one) also uniformly distributed on the collecting plates is often presented as the best design criterion. However, these rules are not of universal validity and selecting the most appropriate discharge electrode for a given application is most important, even more so when wide plate spacing is also involved in the ESP design.

To experimentally assess the electrode selection for different applications and filter configurations, the aforesaid three electrode types have been tested. Figure 3 presents

**FIGURE 2** Fly ash size distribution.

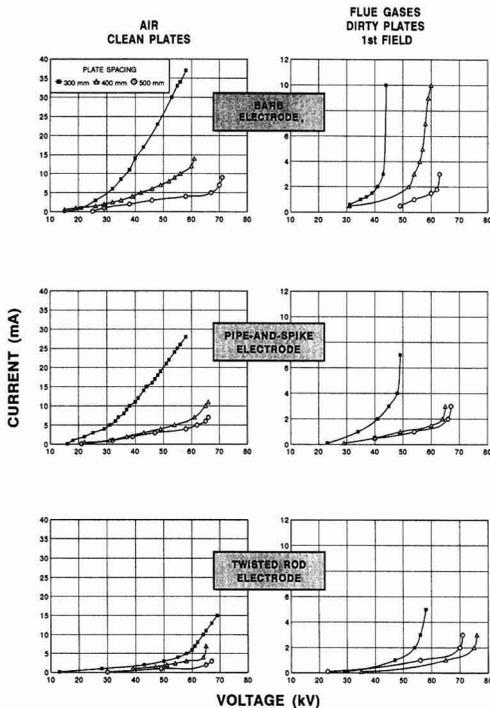


FIGURE 3 Voltage-intensity curves of electrodes.

the voltage-current intensity characteristics for the different electrodes. The reference V-I curves obtained under air load at ambient temperature and clean plates are presented in this figure together with curves obtained under operating conditions with high resistivity ash, as representative of the extreme conditions inside the filter (V-I curves with low resistivity ash are close to reference curves). As can be seen in Figure 3, the characteristics of used electrodes cover the

performance range of commercial geometries, and they can be classified as follows:

- The barb wire is a high energy electrode, low-voltage/high-current producer.
- The pipe-and-spike electrode is a medium energy electrode producing moderate-voltage/moderate-current.
- And the twisted rod electrode is a low energy electrode with typical high-voltage/low-current characteristics.

Figure 3 also indicates the effect of plate spacing on the electrical behavior of electrodes. A wider plate spacing always produces the expected increased voltage coupled with a reduced current. Although in some cases, i.e. using the pipe-and-spike electrodes, the transition from a 400 to a 500 mm plate spacing does not produce a substantial modification of V-I curve.

A remarkable advantage of the use of a wider plate spacing when high resistivity ash is collected lies in the improvement of electrode performance due to suppression or reduction of undesirable phenomena, like back-corona. This is clearly observed in the V-I curves of Figure 3 corresponding to filter operation conditions (dirty plates). Under these conditions of high resistivity, some of the V-I curves show the vertical rise in current typically associated to the establishment of back-corona. Back-corona production is reduced by an increase on plate spacing or by using a lower energy electrode. In accordance with V-I curves, severe back-corona was produced by barb electrodes in a 300 mm configuration, and some evidence of back-corona remains at 400 mm with these wires and at 300 mm with pipe-and-spike electrodes.

ELECTRICAL OPERATING POINTS

The range of operating conditions, in terms of average voltage, mean electric field, and current density, obtained with the tested configurations of PESP are presented in Table 5. As can be seen a gradual modification of electric

TABLE 5. Electrical Operating Points

Coal Type	Electrode Type	Plate Spacing (mm)	Continuous Energization			Intermittent Energization		
			V (kV)	E (kV/cm)	j (nA/cm ²)	V (kV)	E (kV/cm)	j (nA/cm ²)
Coal A	Barb	300	40-47	2.7-3.1	9-51	31-41	2.1-2.7	0.6
		400	59-64	3.0-3.2	11-45	38-44	1.9-2.2	1.0-1.9
		500	66-80	2.6-3.2	4-11	46-51	1.8-2.0	1.3
	Pipe	300	42-48	2.8-3.2	17-47	29-34	1.9-2.3	0.6
		400	57-65	2.9-3.3	8-28	44-49	2.2-2.5	1.0
		500	62-70	2.5-2.8	4-11	45-55	1.8-2.2	1.3
	T. Rod	300	50-56	3.3-3.7	9-21	41-49	2.7-3.3	0.6
		400	63-77	3.2-3.9	3-9	41-54	2.0-2.7	1.0
		500	67-75	2.7-3.0	3-4	43-54	1.7-2.2	1.3
Coal B	Barb	300	47-50	3.1-3.3	28-60	27-32	1.8-2.1	1.9-5.0
		400	60-61	3.0-3.1	8-26	36-40	1.8-2.0	1.0
	Pipe	300	45-47	3.0-3.1	17-38	27-33	1.8-2.2	1.2-1.9
		400	60-62	3.0-3.1	8-26	36-40	1.8-2.0	1.0
T. Rod	300	64-67	4.3-4.5	7-28	43-44	2.8-2.9	0.6-1.9	

sections voltage and intensity, in the way indicated by the V-I curves of Figure 3, is obtained when the gas passages are widening or the discharge electrodes are changed.

Additionally, data in Table 5 also permit the comparison between electrical conditions achieved with standard continuous rectified current and with intermittent energization. For a given PESP configuration, a substantial reduction in operating voltage, and hence of mean electric field, is instantaneously produced when intermittent energization is turned on. As a result, intensity falls up to a nearly constant value, with independence of the used discharge electrode or plate spacing.

COLLECTION EFFICIENCY

The effect of both design parameters - plate spacing and electrode type - on PESP collection efficiency is presented in Figure 4. In this figure, penetration trends obtained with high and low resistivity fly-ash and with each tested PESP configuration using continuous energization are plotted. Two types of data have been considered:

1. Measured penetration for all tested configurations using the same gas velocity (baseline value of 1.1 m/s). This approach implies a variation in the PESP specific collection area (SCA) when plate spacing is modified. Data are representative of the performance of precipitators with the same approximate volume having a different plate spacing. Corresponding SCA values are:

- 300 mm-37.8 m²/(m³/s)
- 400 mm-28.2 m²/(m³/s)
- 500 mm-22.6 m²/(m³/s)

2. Estimated penetration for a constant SCA value in each configuration. A SCA of 30 m²/(m³/s), intermediate between the experimental values, has been selected. In this case, data are representative of precipitators with the same collecting area despite their different plate spacing. Represented figures have been calculated from correlation of experimental values.

From observation of Figure 4, the following information can be extracted:

- The barb electrode, a high-power geometry, produces the best ESP performance when low-resistivity ash is collected and the baseline plate spacing (300 mm) is used; also, as it was expected according to general theory, it gives worse results than the

other electrodes, at baseline conditions, when ash resistivity is high. However, a substantial change in performance is produced when plate spacing is increased. A strong decrease in ESP efficiency for low-resistivity ash is observed when a plate spacing of 400 mm is tested, probably as a direct consequence of associated SCA reduction, whereas a considerable improvement is obtained for high-resistivity ash, despite the aforesaid lower SCA. In this last case, if SCA were maintained a greater improvement in ESP efficiency is predicted.

- The pipe-and-spike electrode gives the best behavior at baseline conditions for high-resistivity ash and the worst for low-resistivity ash. And also performance trends are opposite when a wider plate spacing is used. In this case, the associated reduction in SCA leads to a lower efficiency for a 400 mm ESP processing high-resistivity ash, although predictions indicate a potential efficiency increase for constant SCA. However, it has to be pointed out that a considerable improvement in ESP performance is obtained with low-resistivity fly-ash when plate spacing is increased from 300 to 400 mm with continuous energization.
- The twisted rod electrode, a low-power electrode, tends to produce a similar performance than pipe-and-spike electrode for plate spacings of 300 and 400 mm, giving a bit lower efficiency for high-resistivity ash. This electrode also shows a higher potential for performance improvement when modification of plate spacing from 300 to 400 mm is made maintaining SCA.
- Finally, tests using a very wide plate spacing (500 mm), only performed under high-resistivity conditions, always indicate a degradation of ESP performance with respect to the standard wide plate spacing (400 mm), especially for the twisted rod electrode. When a spacing of 500 mm is used a new reduction on SCA appears and needed voltages are closer to TRs maximum design values by which some limitation on electrical performance can be found (as seems to occur for twisted rod electrode). Avoiding the effect of SCA reduction, pipe-and-spike is the only electrode geometry that shows a performance improvement potential, indicating its ability to efficiently support very wide plate spacing designs with proper ESP sizing.

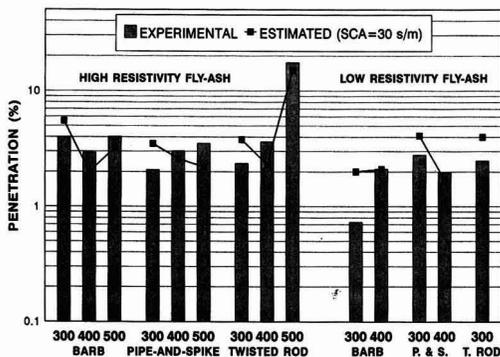


FIGURE 4 Effect of filter configuration on efficiency.

INFLUENCE OF ENERGIZATION ON ESP PERFORMANCE

Although new ESP energization methods, like intermittent wave forms, have been mainly focused to achieve reductions in precipitation power consumption while maintaining performance levels, their effect on efficiency can not be easily predicted without plant testing in real operation conditions. Moreover, the effect of energization is also coupled with the effect of other factors, like electrode type or plate spacing, which have been conceived mainly to affect ESP efficiency or capital costs, but which also have a considerable effect on power consumption.

The global results of the extensive testing of ESP performance using conventional continuous rectified current and intermittent energization are presented in Figure 5. This figure contains experimental data for all the tested ESP

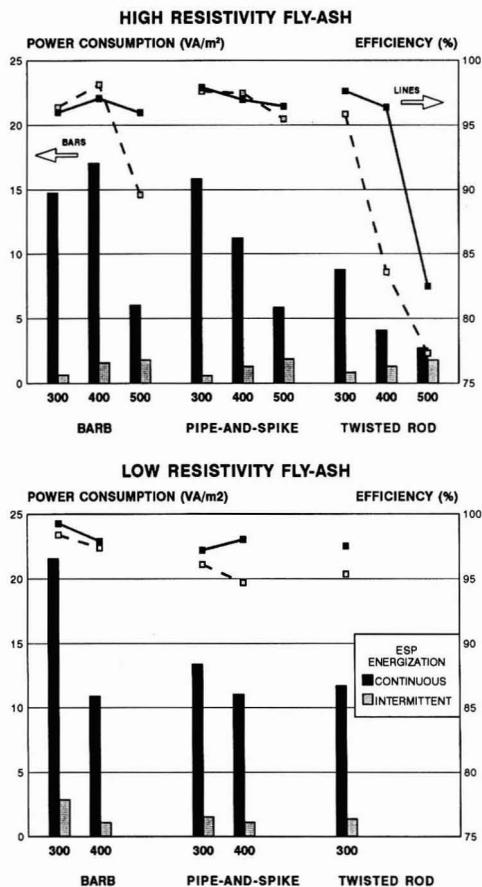


FIGURE 5 Effect of energization on ESP performance.

configurations obtained with the baseline gas velocity and with all ESP fields active.

The most impressive finding is the drastic fall of power consumption with intermittent energization. As indicated in Table 5, intermittent energization reduced the average voltage and especially the secondary current, leading to the low power values plotted in Figure 5. In the case of high resistivity, power consumption with intermittent energization is approximately the same for each plate spacing, independent of the discharge electrode used. Power increases with plate spacing due to the higher average voltage obtained with a wider spacing, while a nearly constant very low current is always produced.

It must also be emphasized that the beneficial effect of intermittent energization on operation cost is associated, in same cases, with a parallel increase of ESP efficiency. Thus, operation of barb electrode is improved in these two ways with high-resistivity ashes, and also pipe-and-spike electrodes can attain some efficiency improvement. However, when intermittent energization is coupled with low-power electrodes, like the twisted rod type, or with a very wide plate spacing, there is a drop in ESP efficiency. Also an unfavorable effect on efficiency is always produced under low-resistivity conditions when using intermittent energization. Graphs in Figure 6 show the direct output of the PESP opacity monitoring system during a change of the ener-

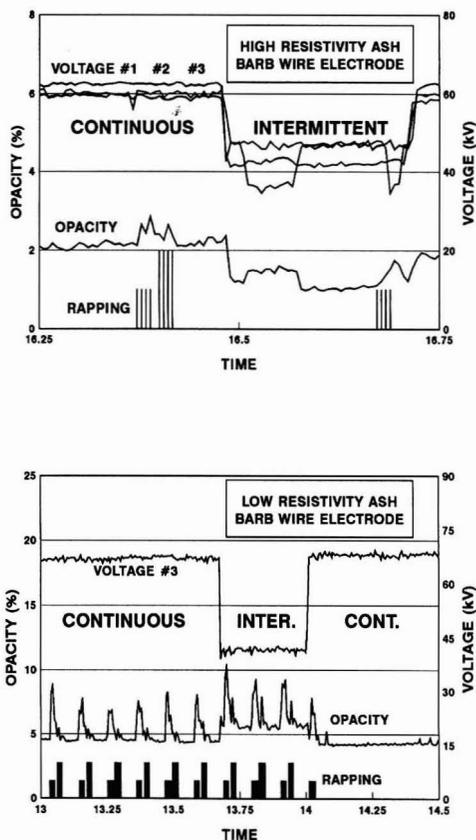


FIGURE 6 Pilot ESP output under different energization modes.

gization under high and low resistivity conditions, using the same discharge electrode. The opacimeter readings plotted in this figure clearly indicate the response of the PESP to changes in the energization and the previously commented effect of intermittent energization on efficiency, positive with high resistivity ash and negative with low resistivity.

In relation to intermittent energization results, it must be pointed out that measured reduction of power consumption in the PESP is higher than measured in the power plant full-scale precipitator. Differences between the control systems of both precipitators, and some evidence of a poor adjustment of the full-scale unit power supply, make difficult to determine the real effect of scaling up on energy savings in coal ESPs. In any case, the need for a fine tuning of energization control has become evident.

Attending to conventional rectified energization results, a clear graduation of power consumption is established between different electrodes, in the expected way according with their electrical characteristics. Moreover, a substantial power reduction is always obtained with wider plate spacings, excepting for the barb electrode operating with high resistivity ash, where a lower power consumption was measured for the spacing of 300 mm. In this situation, PESP operation was strongly restricted by dust resistivity thus imposing a certain reduction in operating voltage in order to control intensity excursions.

CONCLUSION

Results clearly indicate the possibilities of ESP performance optimization in a given application by adequately combining plate spacing, electrode geometry, and power supply, but different criteria are required as a function of energization type and dust properties. Also a different approach may be required for the design of new units and for the retrofitting of existing ones.

The use of intermittent energization appears as one of the most interesting aspects of coal precipitators improvement, although a precise adjustment of operational parameters is needed to ensure its best performance. The intermittent rectified current is always able to strongly reduce ESP power consumption and, under adequate conditions, when dust of high resistivity is involved, it is also able to improve collection efficiency.

In the case of high resistivity ash, moderate and low-power electrodes present the best behavior for a conventional narrow plate spacing (300 mm), whereas high-power electrodes tend to have some advantage when a wide plate spacing (400 mm) is used. This advantage is more intense with intermittent energization. Results also indicate that, in general, a very wide plate spacing (500 mm) tends to produce lower ESP efficiencies than the European wide spacing.

In the case of low-resistivity ash, the conventional design—narrow plate spacing and high-power electrodes—appears as adequate. Results also indicate that some improvement in efficiency could be promoted by substituting this standard configuration for a correctly sized ESP using wide plate spacing and moderate-power electrodes. However, under low resistivity conditions continuous energization is required to achieve a higher performance.

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LITERATURE CITED

1. **Grieco, G. J.**, "Understand, Solve Problems with ESP Wide Plate Spacing," *Power*, pp. 42-48 (August 1994).
2. **Crynack, R. R.**, "Discharge Electrodes for Electrostatic Precipitators—A Perspective". 9th EPRI Particulate Control Symp., Williamsburg, Virginia (October 1991).
3. **Rea, M., V. Bogani**, "Influence of the Electrode Geometry and of the Operating Characteristics on the Efficiency of Electrostatic Precipitators." 10th Particulate Control Symp. and 5th Int. Conf. on Electrostatic Precipitation, Washington, DC (April 1993).
4. **Landman, E. C., et al.**, "Intermittent Energization with High Fly Ash Resistivity". 10th Particulate Control Symp. and 5th Int. Conf. on Electrostatic Precipitation, Washington, DC (April 1993).
5. **Paulson, C. A. J., R. Morrow, A. J. Prokopiuk**, "The Performance of a Pilot-Scale Electrostatic Precipitator Using Continuous, Intermittent and Pulsed Energization". 10th Particulate Control Symp. and 5th Int. Conf. on Electrostatic Precipitation, Washington, DC (April 1993).
6. **Weaver, E. H., F. A. Gallo, S. Mecheri**, "A Comparison of Several Generations of Electrostatic Precipitator High Voltage Control Systems". 9th EPRI Particulate Control Symp., Williamsburg, Virginia (October 1991).
7. **Cañadas, L., et al.**, "A Flue Gas Desulphurization and Electrofiltration Pilot Plant: Design and Objectives". Proceedings of the Florence World Energy Research Symposium FLOWERS'94, pp. 745-763. SG Editoriali, Padova, Italy, 1994.
8. EPA Stationary Source Sampling Methods. "Method 17—Determination of Particulate Emissions from Stationary Sources (in-stack filtration method). Rev. 2. 7/91".
9. **Cañadas, L., et al.**, "Influence of Filter Configuration and Operating Conditions on Performance of Coal Electrostatic Precipitators". EPRI/DOE International Conference on Managing Hazardous and Particulate Air Pollutants, Toronto, Canada, (August 1995).
10. **Cañadas, L., B. Navarrete, L. Salvador**, "Theoretical Modelling of Electrostatic Precipitators Performance (PRELEC Code)." *Journal of Electrostatics*, 34, pp. 335-353, 1995.
11. **Dubard, J. L., and R. S. Dahlin** "Precipitator Performance Estimation Procedure," EPRI, Palo Alto, California, 1987.

Hindcasting Volatile Chemical Emissions to Air from Pondered Recycle Oil

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Because of weathering, while abandoned for over a decade, the floating oil at the site of a former oil recycling operation became depleted of numerous volatile and semi-volatile constituents. The chemical record preserved in the bottom sediment provided the key information from which operating conditions over the period 1973-1982 could be reconstructed. Chemical concentrations in the oil could be determined and coupled with an environmental chemodynamic model to quantifying chemical release rates to air. The oil contained elevated levels of naphthalene. The oil, BTX fraction, several chlorinated solvents, and two PCB Aroclors were modeled. Annual average emission rates were 4000 kg for naphthalene, 840 for TCE, 300 for benzene and 14 for A-1248. Fundamental results obtained are: a) the criteria required for using historic, bed-sediment data to reconstruct key chemical processing information at a former plant site and b) field data on volatile and semi-volatile chemical emission kinetics from deep, floating oil pools.

INTRODUCTION

The waste oil recycler obtains feed material from diverse sources. These can range from gasoline service stations where waste motor oil is available to petroleum refineries where quantities of waste crude, or process oils are obtained to chemical manufacturing plants where solvents and numerous other oil-like liquids are produced. The waste oil recycler is interested in these materials primarily because they can be reused. Reuse as fuels is an attractive market.

Prior to reuse it is common for the waste oil to undergo some form of treatment and blending. During these operations there are opportunities for hazardous constituents to be emitted to the surrounding environment. Although primarily mineral oil they become contaminated with other constituents during their primary use. A recent study [3] classified waste oil into three categories: automotive oil, industrial oil and unknown sources. Potentially hazardous

constituents in these oils include metals, chlorinated solvents and other organics.

The objective of this paper is to present the methodology used and the resulting numerical estimates of quantities of selected hazardous constituents emitted to air from surface impoundments covered with oil (i.e., pondered oil) that are normally associated with recovery and recycling process. In order to illustrate the methodology a site-specific case is used. The operations and conditions at the Combustion Inc. Site in Livingston Parish Louisiana provide these.

THE COMBUSTION, INC. OIL RECOVERY PROCESS

The recovery operations at this site cover the time period of 1964 to 1982. The process evolved with time; it started with a single, small tank truck and a few storage tanks. When it shut down the operation involved several tanker trucks, much process equipment and an elaborate waste water treatment operation. Figure 1 shows the generic features of the operation in its peak years of operation, 1973-1982. This figure illustrates aspects of the over-

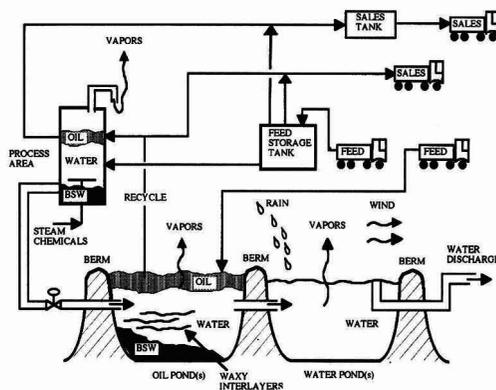


FIGURE 1 Generic schematic of Combustion Inc., oil recovery operation.

all operation that includes the process area, oil ponds and the water treatment ponds.

Waste oil arrived by tanker truck. It was placed into storage tanks in the process area and it was also delivered directly to the oil ponds. Because of water and settleable plus suspended solids admixed with waste oil it is usually unsuitable for most reuse applications. Some degree of treatment is required. In reality the oil ponds serve as a treatment operation. In these ponds the water and solids settle out producing a somewhat clarified oil. The pond-oil may or may not receive further treatment in the process area prior to being placed in a tanker truck and marketed.

In the process area the waste oil was treated with heat, steam and various aqueous solutions containing salts to effectively speed-up and break the water-oil emulsion that normally exist and aid in the separation of water and solid fractions. As illustrated the process treatment vessel produced three layers of materials based on densities; the phases are oil, water and solids. The water contains constituents in solution derived from contact with the oil. The bottom material is a dense ($\rho > 1 \text{ g/cm}^3$) sludge-like substance containing inorganic solid particles of a soils type or otherwise, and a large fraction of comingled oil. This sludge material will be referred to as bottom solids (i.e., BS).

The water and BS accumulated over time in the lower portion of the process treatment vessel. Periodically it was necessary to purge this material from the system. This was done by gravity transfer or by pumping it to the oil pond. Here the BS settled onto the bottom and the water eventually flowed to the aqueous ponds where treatment was performed before its final discharge to a receiving stream. Rainwater entering the ponds was handled likewise through the aqueous ponds.

CHEMICAL STATE OF THE SITE IN 1984

Interest in the Site as a source of hazardous substances commenced in 1984 when it was placed on the National Priorities List. Quantities of dichlorobenzene were reported in the air above Pond H necessitating this action by the US EPA. Thirteen ponds occupying the site in 1985 when an as-

essment study was performed [8]. At that time six ponds, designated A, B, C, F, G, and H contained oil floating on water. Total surface area was 10,400 m² with 4880 m² covered with oil. The volume of oil was estimated to be 1460 m³. Oil thickness varied from 1 cm to 82 cm on these ponds. Water volume was estimated at 5540 m³. Water layer thickness varied from 6 cm to 130 cm. Sludge volume was estimated to be 3230 m³. It varied from 0 cm to 94 cm. Analysis of the contents of the ponds including the floating oil layer, water and "sludge" was performed several times over the period of active site operation which was 1964-1982. This data has been compiled in a single report containing nineteen individual studies over the period 1980-1990 [1]. After being placed on the National Priorities List for clean-up action a preliminary investigative report was performed anticipating site remediation [2]. Prior to remediating the site a study was undertaken to fully characterize all materials remaining in, on and under the surface impoundments [4]. During remediation, which consisted of on-site water treatment and off-site disposal of oil and sludge to a landfill, additional chemical data was obtained on the various media [10].

In general the types and quantities of substances at the site were weathered petroleum hydrocarbons. Composition and quantities are consistent with survey reports on the character of waste oil [3]. Contaminants, in addition to benzene, toluene, xylene and other normal constituents of oil, include polychlorinated biphenyls (PCBs), chlorinated solvents and metals. Of the three categories listed in the Bider et al. Report [3]: automotive oil, industrial oil and mixed or unknown sources, the latter best characterizes the Combustion Inc. oil. A subset of constituents normally found in waste oil was selected to perform air emission calculations; see Table 1. The mean, medium, and maximum chemical compositions represent the mixed or unknown category in Bider et al. [3]. Those used to characterize the Combustion Inc. oil are based on an investigation commissioned by the author [4]. The data are concentrations in oil from bottom sediment samples for the ponds on the site; it represents all the available bed-sediment data from core profile and composite samples: up to thirty-six

TABLE 1. Selected Volatile and Semi-volatile Constituents in Waste Oil ($\mu\text{g/g}$)

Chemical	Mixed or Unknown Sources Used oil Bider et al.			Unweathered Oil Bottom Sediment Combustion Inc.		
	Mean	Median	90th P'tile	Mean	Median	Max
Benzene (B)	1030	30	250	55.4	53.8	161
Toluene (T)	2260	450	4400	163	124	645
Xylenes (X)	4506	600	3000	337	312	1075
Naphthalene	43	10	16	672	484	3120
Benzo-a-anthracene (BaA)	521	330	998	5.4*	5.4*	333 ($n = 1$)
Benzo-a-pyrene (BaP)	94	12	60	5.4*	5.4*	5.4*
Polychlorinated biphenyls (A-1260)	72	6	50	25.9 [†]	25.2 [†]	39.2 [†]
1,1,1-Trichloroethene (TCE)	2630	300	3400	10.8	10.8	10.8 ($n = 3$)
Trichloroethene (TCE)	1198	100	1600	170	43	253
Tetrachloroethene (TTCE)	1237	170	1300	54.3	37.6	355

*BQL (below quantitation limit); minimum detect used.

[†]Floating oil values.

observations were available on many of the substances. The oil content of the BS varied from 18.6% to 33.1% by weight. The lower value was used to ratio the concentrations to a solids-free basis; this means the measured values were multiplied by 5.38 (i.e., $1/.186$) for Table 1. Two of the eleven constituents in this pond bottom sludge were below the quantitative limit of detection for the chemical analysis protocol used; in this case the minimum detectable concentration limit was used.

In contrast, the composition of numerous organic chemicals in the floating oil was unlike that reported by Bider et al. for waste oil [3]. Of the volatiles only a few samples contained concentrations above the quantitation limit ($\sim 1 \mu\text{g/g}$). The average concentration ratios in floating oil to the average values in Table 1 for Combustion Inc. were 0.09, 0.04, 0.04, 0.03 and 0.04 for B, T, X, TCE and TTCE, respectively. The PCB, Aroclor 1260 was present above the quantitation limit in Ponds B, C, F, G, and H, these ranged from 19.4 to 36.1 $\mu\text{g/g}$. For the base/neural constituents BaA was found in a single sample at 61 $\mu\text{g/g}$ in the surface oil of Pond C; all others $n = 42$ were BQL. Naphthalene and BaP were below the quantitation limit in the floating oil of all six ponds. This general lack of all volatile and some semi-volatile constituents suggests that the floating oil had weathered significantly in the approximately eight years the site was inactive. It is inappropriate to estimate volatile chemical emissions for the 1973–1982 time period based on compositions in the remaining floating oil in the ponds.

INFORMATION FROM BOTTOM-SEDIMENT RESIDING CHEMICALS

A search for unweathered or otherwise unaltered quantities of oil representative of the site during the time period of active operation eventually led to a detailed investigation of the chemical make-up of accumulated sediments on the bottom of the oil impoundments [4]. Chemical profiles in freshwater lake and marine bed-sediment have been used extensively to track and quantify anthropogenic input into aquatic systems over decades of time [6, 7]. Typically, unreactive species such as 210 Pb or very slowly reactive species such as PCB have been used. An extensive bed sediment coring project was planned and executed in October 1992.

In addition to finding some unweathered oil the bottom sediment coring with subsequent sectioning and chemical analysis could potentially yield other useful information. For example the sediment constituents may contain a "fingerprint" revealing quantities of unusual hazardous materials delivered to the site. If a sediment deposition rate is established the time of occurrence of unusual inputs can be established. In addition, the time-history of the changes in the character of waste oil delivered and processed at the site is revealed.

For sediment chemical profile data to be useful for such purposes several things must occur: 1) The sediments delivered must be reflective of the waste oil operation both in the pond area and the process area; in other words there must be a direct link between the source of chemicals and the arrival of sediment particles on the bed surface. 2) Sediment solid particles must retain quantities of oil material attached onto the surface, settle rather quickly (days to a week) and consolidate with other particles to form a stable

bed of soil-like solid material. 3) The time of delivery of oil laden solid particles should reflect the proper chronological order of events in the pond or process area. 4) Baring molecular diffusion of individual chemical species no mixing of layers should occur after particles are in place and have consolidated. 5) There must be no significant reaction of or between chemical constituents in the bed. This includes chemical and/or biological degradation, solubilization by water and out migration, dissolution into the overlying water.

All of the above criteria appear to have been met at the Combustion Inc. Site. A pipeline delivered oil and BS from the process area tanks to Pond C, primarily. Tanker-trucks off-loaded directly into some of the ponds H(?). Soil-like solids (i.e., clays, silts, sands) attract and retain large quantities of oil which they contact. Settling of these particles occurs fairly quickly, particularly the larger diameter pieces as does consolidation. The soil-like particles typically have densities of 2.4 to 2.6 g/cm^3 so that oil, with density 0.8 to 0.9 g/cm^3 , does not preclude their settling if it is present in the 18 to 30% (wt) range. Consolidation is the natural process of the upward expression of water as the soil particles in the bed become more compact with time. Once in place, physical mixing of the bed causing a blending of concentration between adjoining layers is absent. Surface winds and in-pond water currents could move surficial sediments about however extensive scour and re-deposition is not indicated. The stable delta formed at the discharge point into Pond C is evidence of this. A fan shaped deposit, deep at the entrance and thinning with distance suggests once in place wind and water currents were not strong enough to move material about. Oil on the surface of the water column protected it from the direct impact of the wind thereby dampening its usual effect. Only rainwater falling onto the pond surface would induce water currents, these being much milder than those possible if a larger watershed fed the pond. Molecular diffusion may account for some chemical intermingling between layers. For a layer 5 inch thick 16 years is required for an approximate 20% blending with adjoining layers. This is a molecular diffusion based calculation using benzene as the mobile species. Molecular diffusion in liquid filled porous media is known to be a slow process. The low permeability of the clay that forms the bottom of the ponds and the shallowness of the water hydraulic gradient in the ponds rules against significant downward water percolation and solubilization of chemicals from the bed. These organic chemicals, present as a mixture, are not reactive chemically but are known to remain stable chemically for centuries as in most buried oil deposits. The oil content is too high and the chemical make-up is too toxic for microorganisms survival so that any significant biodegradation of species may be discounted [5].

Clear Schedule 40 PVC pipe, $1\frac{1}{4}$ to 2 inch diameter, was used to obtain pond bottom sediment samples for chemical profiling. Such samples were obtained at four locations in Ponds B, C, F, G, H and I. Due to cost considerations only three of four cores in Pond C, H and I were analyzed. The others were placed in refrigerated storage but were eventually lost when the commercial laboratory changed ownership.

The cores were obtained by pushing the pipe through the surficial sediment and approximately six inches into the clay below. The pipe was protected from contamination by

a plastic film as it moved through the oil layer and water layer. The clay seal on the bottom, clearly distinguishable from the oily sediment, aided in preventing sample loss during retrieval. A plastic end-cap on top of the pipe created a vacuum further aiding retrieval. Another plastic end-cap was placed on the bottom. All cores were stored and transported in upright vertical position. Samples were immediately transported to the analytical laboratory under chain-of-custody. Core "slicing" was performed with the tube in a vertical attitude. A section of sediment of known length was spooned-out and placed in appropriate containers. The exposed pipe was sawed away prior to spooning out the next "slice" of core.

Quality Assurance/Quality Control (QA/QC) procedures performed for the analyses of the samples included analysis of field blanks, duplicates, matrix spike and matrix spike duplicate samples. All procedures were performed in accordance with SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, USEPA 3rd Edition, Revised No. 1986.

CORE PROFILE RESULTS AND DISCUSSION

Core length shortening is a potential problem with the pipe retrieval technique used. Within the tube, due to friction drag by the solids along the inner wall, the core is compressed. Distances upward from the clay interface were undoubtedly lessened in the core sediment than in the pond sediment. No precise percentage shortening was determined. Previous sludge depth probing with rods [8] suggest that the shortening was not excessive since depths of the "sludge" layer were comparable with core sample lengths. Since chemical partitioning is very strongly favored in the oil phase and concentrations are low in the adjoining porewater it contains only minute quantities. Any water expressed during core compression will have an insignificant contribution depleting the quantity of chemical thereby lowering the measured concentration in a given "slice." When placed on a weight fraction basis (i.e., $\mu\text{g/g}$ solid) the chemical concentration should be nearly identical with the undisturbed column. Only concentrations based on volume of sediment/water mixture or volumetric accumulation rates (i.e., bed accretion rates) are comprised by core compression.

Previous studies of "sludge" depth in the ponds indicated that Pond C contained a significant accumulation. It was also suspected to be a prime recipient of waste solids and water from the process area. This being the case a core (Location 1) was obtained near the presumed waste inlet point. Of all potential sample points its accumulation of solids best reflects occurrences in the process area. Figure 2a, 2b and 2c contain selected chemical concentration profiles measured in this core. Measuring up from the bottom of the tube, the clay-soil/sediment interface is 1.12 feet and the sediment/water interface is 3.83 feet. The years indicated in Figure 2a denote the start and end date of the use of Pond C.

The volatile chemical species will be considered first. The profiles of benzene, toluene and total xylenes are similar in shape. A low concentration layer is present at about $1\frac{1}{2}$ ft. below the sediment-water interface. This variation likely reflects the quality changes over time of the waste materials received. The profiles of the chlorinated species, TCE

and DCB (dichlorobenzene) are shaped differently. In these the minimum concentration occurs at 2 feet below the S/W interface as does the total chlorinated hydrocarbon concentration. The latter profile shows an increasing concentration from approximately 1975-1982 suggesting the site was handling relatively more of this type material.

These profiles shapes suggest two aspects concerning chemical mobility in the bed sediment. First, mixing at this location over the past fifteen plus years, including the seven since operations ceased, has been very slow. Even a modest amount of mixing in the sediment column should have resulted in a blending of the layers producing a profile with uniform concentration. Second, the surface layer nearest the S/W interface displays no depletion of any volatile species; this indicates little or no solubilization with subsequent transport to the water column. Both these interpretations suggest a general lack of chemical mobility after placement on the bottom of Pond C.

As noted above the oil content of the bottom sediment ranged from 18.6 to 33.1% (wt). This fraction is within the range of fossil fuel bearing, liquid hydrocarbon contents of sandstones. Such high oil contents effectively render the volatile chemical species, such as BTX, resilient to microbiological degradation due to its toxicity to the organisms [5]. This being the case the concentrations in the oil fraction of the bed sediment should be identical both in quality and quantity to the oil processed at the site during its operational period. To place the concentration on an oil basis the numerical values in Figure 2 need be increased by 3 (i.e., $1/.331$) or 5.4 (i.e., $1/.186$). This latter value was used to yield the data in Table 1.

The semi-volatile species concentration profiles in Figure 2 include naphthalene, phenanthrene and 2-methyl naphthalene as representative of this group. The concentration trend through time is a decreasing one; values in 1982 being 43 to 49% lower than the high at around 1975. This trend likely reflects gradual changes in the characteristics of the oil waste brought to and processed at the site. It is noteworthy that Combustion, Inc. waste oil contained naphthalene in concentrations that exceeded those reported in the Bider et al. compilation [3]. This fact possibly reflects high naphthalenic contents of the source oils in the region.

The metal species concentration profiles in Figure 2 include lead (Pb) and zinc (Zn) as representatives of this group. The latter shows no discernable trend through time. However, the lead content decreases dramatically; it does so faster than the naphthalenic fractions. The 33% reduction from the maximum at depth may represent, in part, the phase-out of its use in gasoline which commenced in 1974.

Chemical concentration profiles were analyzed at two other locations (3 and 4) in Pond C. These were generally on a transect at increasing distances away from the waste inlet point. Types of species and concentrations were much like those at Location 1. The thickness of the "sludge" layer was slightly less at those locations. Whereas the "sludge" was almost three feet deep in Pond C it was less than one foot in Pond H and I. This allowed less slices to be obtained for profiles in order to satisfy the quantification limits of the analytical equipment. In general the same species in roughly the same concentration ranges were observed. For example maximum benzene concentrations were measured at Location 1, Pond H and Location 4, Pond I; these were $15 \mu\text{g/g}$. Lead was present in Ponds H and I also; its

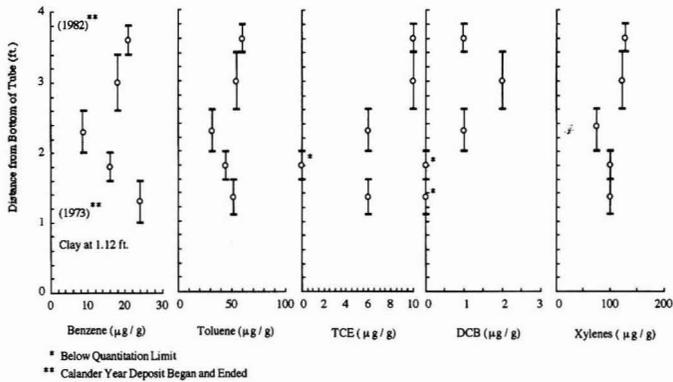


FIGURE 2(A) Concentration of chemicals in Pond C, Location 1.

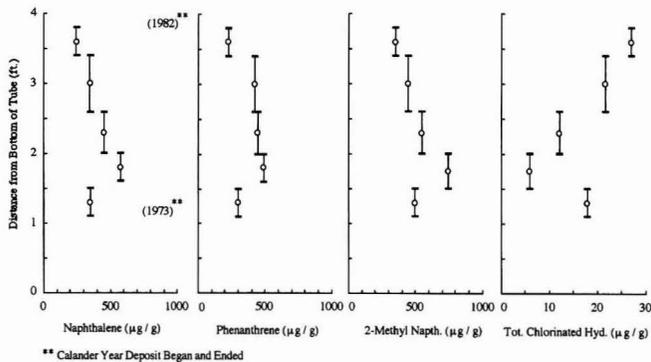


FIGURE 2(B) Concentration of chemicals in Pond C, Location 1.

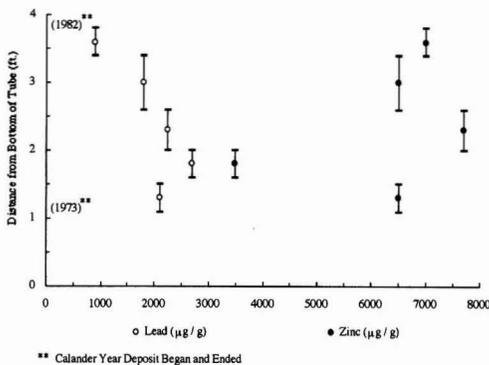


FIGURE 2(C) Concentration of chemicals in Pond C, Location 1.

maximum for these were 1370 $\mu\text{g/g}$. Due to the reduced number of sediment "slices" at locations on Ponds H and I no discernable time-trends in concentrations behavior was possible.

In general the investigation of the pond bottom sediment revealed a source of unaltered waste oil containing chemical concentrations reflective of the site during its operational period. The data is shown in Table 1.

CHEMICAL TRANSPORT AND REACTION PROCESSES IN POND SYSTEM

The ponds served both a storage and treatment function. The oil-covered ponds were used for temporary oil storage. It arrived by pipeline from the process area or was delivered there by tanker truck. It departed in a like manner, however, some oil remained on the surface. Undoubtedly while floating on the surface some large pieces of suspended particles settled from the oil layer and came to rest on the bottom of the ponds. In effect this is an oil treatment operation, however, the heating-chemical based operation in the process area was much more efficient in this regard.

Solids removed from the oil in the process area were delivered to the oil ponds. Pond C was the usual recipient. Until the pond was cleaned out settleable solids with oil attached was stored in the ponds. At the time of closure, ponds A, B, C, F, G, and H contained oil floating on the surface. These ponds are depicted as one in Figure 3. Ponds J, K, L, M and N contained little or no oil, these are depicted as the one water ponds in Figure 3.

Water entered the system by inputs from the process area and by rain falling upon the surface. Floodwater topping the berms may be another input but these were not considered in this study. Water, contained in the tank-bottom waste solid-slurry was pumped or otherwise delivered to the oil ponds. By the use of weirs the water from underneath the

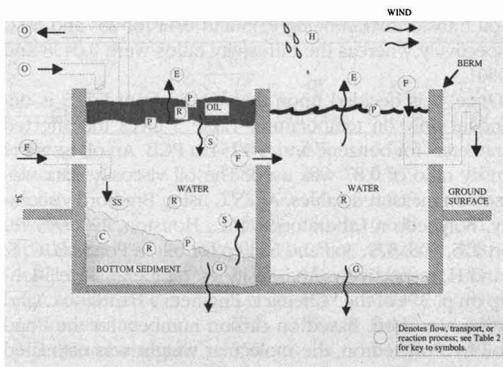


FIGURE 3 Generic schematic of Combustion Inc., oil, water, solids separator and treatment system.

floating oil exited and entered the water ponds. Generally the weirs seem to operate satisfactory. Suspended matter in this stream would have the opportunity to settle out in the water ponds. While in the pond selected chemicals underwent a degree treatment. Another weir placed at the exit of the water pond allow water discharges to the receiving stream.

Flows of oil to and from the ponds was highly variable within short time-periods of days or weeks. The same applies to the flow of water. This includes rain upon the surface. If longer time-periods are considered, months to a year, the process flows can be averaged and conditions can be assumed to be quasi-steady state. In this model of operation the process flows can be quite variable; however, from the pond operation perspective, a slowly changing or near-steady inventory conditions of oil water solids better characterizes this system. Hence the concept of quasi-steady state allows the establishment of constant or base concentration condition. This condition normally occurs, however, it can be perturbed by using higher or lower concentration conditions. This model of the pond system is employed.

Numerous chemical transport, reaction and flow processes are depicted in Figure 3. Table 2 lists & indexes those shown in the figure. Some of these, such as consolidation and chemical reactions, were covered in a previous section. Although it may be occurring to some degree chemical movement underneath the pond system by groundwater or other processes will not be considered since it is of no relevance to the evaporative processes. The only process that will be quantified in detail is chemical evaporation from oil into the atmospheric boundary layer. Chemical solubilization into water which is in part driven by rainwater entering the system, and chemical partition (equilibrium) between media such as that between the oil/water, bottom-sediment/water and water/air phases although occurring in the pond system will not be considered in this document.

CHEMICAL VOLATILIZATION MODEL FOR OIL PONDS

The process by which volatile chemicals move through a liquid phase emerge at the interface and enter the air has received extensive study [9]. This includes the liquids wa-

TABLE 2. Flow, Transport and Reaction Processes within the Pond System

Symbol	Definition
O	Oil transfers between pond and process
F	Water and waste flows in and between ponds
SS	Solid settling
C	Bed consolidation
H	Rainwater input
R	Chemical and biochemical reactions
S	Chemical solubilization to water
G	Chemical movement to groundwater
E	Chemical volatilization
P	Chemical partitioning between phases

ter and oil. The flux equation, which expresses the rate of chemical transport for species A is:

$$n_A = {}^1K'_{A4}(\rho_{A4} - \rho_{A4}^*) \quad (1)$$

and

$$1/{}^1K'_{A4} = 1/{}^1k'_{A4} + \frac{c_4 RT}{\gamma_{A4} P_A^*} / {}^4k'_{A1} \quad (2)$$

where n_A is the flux in mass $A/L^2 \cdot t$

${}^1K'_{A4}$ is the overall transport coefficient, L/t

ρ_{A4} is the concentration in oil, mass A/L^3

${}^1k'_{A4}$ is the oil-phase transport coefficient, L/t and

${}^4k'_{A1}$ is the air-phase transport coefficient, L/t .

The remaining group of terms in the inverse of Henry's constant, H_p in L_{oil}^3/L_{air}^3 , for the equilibrium distribution of A between the phases;

$$H_p \equiv \gamma_{A4} P_A^* / c_4 RT \quad (3)$$

Here γ_{A4} is the activity coefficient for A in the oil phase, dimensionless; P_A^* is the vapor pressure of A , T is the temperature at the interface, R is the gas constant and c_4 is the molar density of the oil. If the atmospheric boundary layer contains A of concentration ρ_{A1} , in mass A/L_{air}^3 , then $\rho_{A4}^* = \rho_{A1}/H_p$. In order to maximize the flux the concentration of volatile species in air will be set to zero, therefore $\rho_{A4}^* = 0$ in all subsequent uses of the expression. Equation 2 is resistance-in-series mass-transfer model commonly used for the transport of a chemical species between phases.

In addition to the concentration of the volatile substance in the oil, ρ_{A4} , the algorithm represented by Eqs. 1, 2 and 3 accounts for environmental parameters, wind velocity and temperature, and physicochemical parameters. Since many of these parameters are quite variable depending upon the conditions chosen, they are discussed in the following paragraphs. In all cases the parameters chosen tended to maximize the emission rate.

After studying meteorological records in the Baton Rouge area 25°C (77°F) and 60°C (140°F) were chosen as average and maximum liquid temperatures for the ponds. Values of 1.3 m/s (3 mi/h) and 5.4 m/s (12 mi/h) were chosen for the wind speed range. Using a correlation developed for surface impoundments, water-side coefficients on ethyl

ether, values of 1.0 and 2.7 cm/h were obtained for the two wind speeds. A similar correlation for the air-side coefficient on water was used to obtain values of 1055 and 4220 cm/h for the same wind speeds. Based on a molecular weight characterizing the VOCs, which were generally larger molecules, and using Graham's law the above values were reduced by 40% to 0.4 and 1.1 cm/h for the water-side and 400 to 1700 cm/h for the air-side coefficients.

The primary environmental factor that effects chemical transport within the oil is the wind. Due to its interaction upon the surface, oil at depth is brought upward in a mixing motion to replace that from which the volatiles were partially depleted. The oil mixing is characterized by the transport coefficient $^1k_{A4}$. Due to its relatively high viscosity oil is not mixed as efficiently by the wind as water. Although volatile chemical evaporation from thin oil layers, such as slicks on the ocean, have been studied [9], general correlations for a deep liquid pool are available for water only.

Based on established mass-transport principles data on fluid-phase coefficients, k_A , are well correlated using the following dimensionless groupings of parameters:

$$N_{Sb} = aN_{Re}^n N_{Sc}^{1/3} \quad (4)$$

where N_{Sb} the Sherwood number is $k_A b/D_A$, N_{Re} the Reynolds number is vb/ν and N_{Sc} the Schmidt number is ν/D_A . The observable parameters are b , v , and ν which represent fluid depth, velocity and kinematic viscosity; D_A is the molecular diffusivity of the volatile species in the fluid which is also viscosity dependent. The parameter n reflects the response of the coefficient to fluid velocity.

Momentum is conserved through the air-fluid interface; this allows the use of equality of shear stress across the boundary and the liquid velocity is replaced by its equivalent wind speed. A ratio of transport coefficients, oil-to-water, is formed from Eq. 4 to yield:

$$k_{A4}/k_{A2} = (D_{A4}/D_{A2})^{2/3} (\rho_4/\rho_2)^{(n-2)/6} (\mu_2/\mu_4)^{n-1/3} \quad (5)$$

Here depth and wind speed cancel out and $\nu \equiv \mu/\rho$ is used in the transformation. The subscript 4 represents the oil and 2 represents water. So, by use of this equation available values on water-side coefficient can be converted to oil-side coefficients needed in Eq. 2. The major contributor to the water-to-oil transformation is the diffusivity ratio term. Reported values of n were considered for use in Eq. 5. Large values 0.8 to 1.0 yielded unrealistically low transport coefficients; lower than stagnant molecular diffusion!. A value of $n \approx 0.2$ yielded unduly high values since it represent a water-like surface. A value of $n = 1/2$ was accepted as representative of oil. The density and viscosity ratio terms,

which contain n , contribute in a minor way to the water-to-oil transformation being 0.38 and 0.44 for 25° and 60°C respectively whereas the diffusivity ratios were 0.0458 and 0.0801.

Once n is decided upon the k ratio from Eq. 5 is dependent only on temperature; Table 3 gives the affected parameters for benzene and A-1254, a PCB. An oil-to-water density ratio of 0.87 was used. The oil viscosity data was based on measured values. At 25°C using Bradford viscometry, Polyhedron Laboratories, Inc., Houston, TX 1993 report 275, 308, 379, 368 and 623 cp for oil on Ponds B, C, F, G and H, respectively. A viscosity vs. temperature relationship on p. 374 of the "Chemical Engineer's Handbook," 3rd edition was used. Based on carbon numbers for the Pond C oil by Polyhedron, the molecular weight was estimated to be 464 g/mol.

The oil-side coefficients, based on the Eq. 5 transformation, are 0.007 and 0.019 cm/h at 25°C for wind speeds of 1.3 and 5.4 m/s. Similarly they are 0.014 and 0.039 cm/h at 60°C for the same wind speed values.

A field experiment using fresh Louisiana crude oil supplied by the Baton Rouge Exxon Refinery was conducted in a large steel pan on Little Sand Island in Mobile Bay [11]. The evaporative surface was 6.1 m by 6.1 m with 50 cm water and 6.2 cm oil. Winds ranged from 2 to 5 m/s and the oil temperature increased from 27 to 50°C over the test period. Based on benzene concentrations in air, measured at 1.9 cm above and in the center of the square, and extrapolated to the 36 cm oil depth in Pond C the effective transport coefficients were 0.69, 0.10 and 0.47 cm/h over the period. Based on measured benzene concentrations in the oil the coefficient was 0.19 cm/h.

Over the course of the field test, which lasted 7.75 hours, large quantities of low molecular weight hydrocarbons, including four normal alkanes, pentane, hexane, heptane and octane, vaporized. The overall volume reduction was 15% over the test period. Even though this test was performed with a light, fresh crude oil with 35.6 API gravity (0.847 density) of unknown viscosity, that is unlike used oil, it does provide field-scale transport coefficients which are supportive of those estimated for heavier, more viscous oil in Pond C. In addition for small evaporative surfaces the coefficients are known to be higher than for large evaporative surfaces. Using a standard area correction factor [9] for this steel pan and Pond C areas reduces the observed coefficients by 0.78 to 0.84.

It is now possible to complete the calculation for the overall transport coefficients for each volatile and semi-volatile species using Eq. 2. Conditions in the daylight hours when the oil is very warm and the wind speed is highest will dominate and control the flux on a daily basis. During the night time winds are usually calmer and conditions are cooler, generally. For this reason the highest estimated co-

TABLE 3. Viscosity and Diffusivity Data

Temp. (°C)	Water Viscosity (cp)	Benzene Diffusivity in Water (cm ² /s)	A-1254 Diffusivity in Water (cm ² /s)	Oil Viscosity (cp)	Benzene Diffusivity in Oil (cm ² /s)	A-1254 Diffusivity in Oil (cm ² /s)
25	0.894	1.06E-5	0.624E-5	308	1.04E-7	6.12E-8
60	0.469	2.26E-5	1.33E-5	70	5.12E-7	3.01E-7

TABLE 4. Oil Evaporation Parameters

Chemical	$\frac{c_4 RT}{\gamma_{A4} P_A^*}$ (l_{air}/l_{oil})	P_A^* (mm Hg)	${}^1K'_{A4}$ (cm/h)	$\tau_{1/2}^*$ (d)
Benzene	196	397	0.039	81
Toluene	388	200	0.039	81
Xylene	1550	50	0.039	81
Ethylbenzene	1550	50	0.039	81
Naphthalene	43, 200	1.8	0.020	158
1,1,1-Trichloroethane	117	470	0.039	81
Tetrachloroethane	529	104	0.039	81
Trichloroethane	550	100	0.039	81
1,2-Dichlorobenzene	550	10	0.035	90
A-1260	4.83E6	1.31E-3	3.5E-4	25 years
A-1248	3.66E5	1.73E-2	4.2E-3	2.1 years

*Numerical values $\times 3$; see text.

efficient for Pond C will be used for ${}^1K'_{A4}$, being 0.039 cm/h. It represents 60°C and 12 mi/h conditions. Because the assumed conditions of temperature and wind are so extreme an over estimate of the flux for an eight-hour, nominal daylight period will result. For this reason the eight hour flux is taken to represent the average daily emission rate. Table 4 contains a list of volatile and semi-volatile compounds along with the computed overall transport coefficient, ${}^1K'_{A4}$, and other pertinent evaporative parameters. Activity coefficients were provided by D. D. Reible (personal communication 1994). Values of 0.513 were used for the hydrocarbons, 0.725 for the chlorinated solvents and 6.3 for the Aroclors. Vapor pressures reported by Montgomery and Wilkon [12] were used and extrapolated to 60°C.

The results presented in Table 4 show that the oil-phase transport coefficient controls the evaporation for the hydrocarbons and the chlorinated solvents. This is based on the fact that ${}^1K'_{A4} \sim {}^1k'_{A4}$ for these substances. Only for the PCB's, which have very low vapor pressures in comparison, is the air-side resistance controlling. The last column contains evaporation half-life for each consistent in the oil.

The equation for half-life based on oil depth, b_4 , and the overall transport coefficient is

$$\tau_{1/2} \approx 0.7 b_4 / {}^1K'_{A4} \quad (6)$$

An oil depth of 36 cm was used. The numerical values in the last column indicate that the hydrocarbons and chlorinated solvents will be lost in a batch operation within a few months. When oil was continuously added and removed from the ponds the half-life is only a relative indicator of evaporation time.

Soon after operations at the Combustion Inc. site were discontinued the volatile species would be quickly lost as noted above. In fact, with minor exception, all the samples taken during the post operation period indicate these substances are present at or below limit of detection. In 1983 Toxicon Laboratories, Inc. reported 4 to 6 mg/kg of A-1242 and A-1260 in "sludges" of Ponds A, C, F and H [8]. In 1992 A-1248 was below the quantitation limit for the oil in Ponds A, B, C, F, G and H; for A-1260 the values ranged from 19.4 to 39.2 mg/Kg [4]. Table 5 contains these data and other historic data from the Combustion Inc. site. The source of some of this data is unclear and selected numerical values are problematic. Taken as a whole, this reported data is consistent with the model results in Table 4. The lower chlorinated Aroclors, A-1242 and A-1248 should be essentially gone from the oil while A-1260, with low evaporation characteristics, should still be present. Assuming the benzene data in Table 5 is correct the change in concentration from 1980 to 1985 is consistent with a ~ 200 day evaporation half-life while the change from January 1985 to August 1986 is consistent with an ~ 80 day evaporation half-life. The model derived half-life for benzene in Table 4 is 81 days. In summary, the historic data collected at the Site for benzene and A-1260 is in harmony with the proposed volatile emission model.

CHEMICAL EMISSIONS TO AIR FROM OIL PONDS

In order to attempt a general characterization of chemical concentrations in the oil ponds composite samples were obtained. At five locations, spaced to represent equal ar-

TABLE 5. Historic Data for Benzene and A-1260 Concentrations in Pond Oil (mg / kg)

Date	Pond	Laboratory	Benzene	A-1260
7/80	pit (?)	?	1175.8	NR
10/83	?	?	NR	0.003-0.006
01/85	pit	?	0.55-1.6	NR
02/85	B	Toxicon	1.6	NR
	G		4.4	NR
08/86	oil pit	Ethyl Corp. Anal. Lab	0.01-0.02	NR
10/86	B,F,H	Rocky Mountain Anal.	NR	~ 50 (PCBS)
06/87	B	?	NR	47
	C	?	NR	31
	F	?	NR	53
	W	?	NR	69
	10/92	A-H	ERT Laboratory	BQL

NR = not reported. BQL = below quantitation limit.

TABLE 6. Composite Sample Results Combustion Inc. Site
Oil ($\mu\text{g/g}$)

Chemical	Mean	Median	Maximum
Benzene	67.5	51.3	162.0
Toluene	29.6	5.4	97.2
Xylene	107.0	5.4	340.0
Naphthalene	838.0	670.0	1674.0
Benzo-a-anthracene	5.4	5.4	5.4
Benzo-a-pyrene	5.4	5.4	5.4
Polychlorinated Biphenyl	5.4	5.4	5.4
1,1,1-Trichloroethane	5.4	5.4	5.4
Trichloroethane	90.9	81.0	205.0
Tetrachloroethane	53.8	67.5	86.4

eas, in Ponds B, C, F, G, H and I grab samples of the bottom sediment were obtained [4]. These five were then mixed together to create the composite prior to performing the chemical analysis. Table 6 contains the concentration data. All reported values were corrected, multiplied by 5.4, to represent 18.5% oil content. In the opinion of the author the mean, median and maximum values based on the composting process did not accurately portray the oil material in the ponds. Either due to the grab sampling and dilution process or analytical chemistry problems with the soil-like sediment matrix, or other unknown factors the concentrations obtained are at odds with those in Table 1 which reflect many more individual samples. In general the values in Table 1 are higher than those in Table 6. It should be noted that except for naphthalene, the means and maximum concentrations in Tables 1 and 6 are generally significantly less than the means and 90th percentile values reported for used oil from mixed and unknown sources. A combination of the high mean values selected from Tables 1 and 6 is likely more representative of the pond oil character at the site during the operational period. These appear in Table 7.

The mean values of oil volatile and semi-volatile constituents in Table 7 is assumed to represent all six oil ponds. Rather than treat each pond individually all will be lumped together as a unit representing 4880 m² of total surface area. The emission rate is the flux, Eq. 1, multiplied by the surface area:

TABLE 7. Average Annual Concentration and Emission from Oil Ponds

Chemical	Concentration (mg/Kg)	Emission Rate (kg/y)
Benzene	67.5	330
Toluene	163	800
Xylene	337	1700
Naphthalene	838	2130
Benzo-a-anthracene	5.4	2.9
Benzo-a-pyrene	5.4	2.9
A-1248	25.9	14
A-1260	25.9	1.2
1,1,1-Trichloroethane	10.8	53
Trichloroethane	170	840
Tetrachloroethane	54.3	270

$$w_A = A^1 K'_{A4} \rho_A \omega_A \quad (7)$$

where w_A is the rate in mass/t, A is the surface area, L^2 , ρ_A is the oil density, mass/L³, K'_{A4} the overall transport coefficient, L/t, and ω_A is the concentration of A in the oil, mass A/mass oil.

The calculated results appear in Table 7. Numerical values are obtained from the algorithm w_A (kg/y) = 127 ω_A K'_{A4} with ω_A in mg/kg from Table 7 and K'_{A4} in cm/h from Table 4. The coefficient values of BaA and BaP were assumed to be equal to that of A-1248.

The emission rates in Table 7 are in kg/y for each chemical species. These are the average annual vaporization rates to air from the surfaces of oil ponds. The concentration data base does not allow emission rates to be made on another time-scale. An attempt was made to obtain concentrations on a smaller time-scale by profiling the bed and ascribing a year-date to each layer. The data in Figures 2a and 2b shows a typical result. Although there was clearly some concentration variation in time, see benzene for example, so that a rate based on approximate 2-year time periods could have been made. Such concentration details are available for only one location in Pond C. Composite samples representing average values for the nine year operational period were the only data available for Ponds A, B, F, G, and H. For this reason the rate data is reported on a yearly basis, however that for each year of the nine is identical.

Based on Eq. 7, it is seen that high concentrations in the oil will result in proportionally higher emission rates. In addition to the mean concentrations listed in Table 7, maximum values for each chemical species are contained in Tables 1 and 6. It is realistic to assume that during some portion of year for an unknown period of time one or more ponds contain constituents at their maximum concentrations. This being the case the average annual emission rate will be larger than reported in Table 7. Generally, taken together as a whole, the maximum concentrations are three times larger than the mean values; so will the rates be.

CONCLUSIONS

Oil floating on the surface of six ponds in 1992 was essentially depleted of volatile and semivolatile constituents.

Criteria, procedures and limitations were developed for obtaining and using pond bottom sediment to characterize oils handled and/or processed at the Site during the operational period.

Oil-laden bed sediment was extremely stable over the time of interment; being un-mixed with layers above or below; showing no significant surface depletion of water soluble fractions and existing in a state that precludes reactive degradation or downward leaching of constituents.

The concentration signature of the bottom-sediment derived oil was like that reported for similar operations. In general the concentrations of constituents, except for the naphthalenes, were on the low side of those reported by Bieder et al. which characterized used oil from mixed or unknown sources.

Volatilization is the most significant pathway for chemical movement from the oil ponds. Chemical solubilization in water, both process derived and rain derived, is a relative minor pathway for chemical movement from the oil ponds.

A predictive chemodynamic model developed for making emission rate estimates to air during the operational period is in harmony with one field-scale experiment and mimics the behavior of volatiles, semi-volatiles and non-volatiles in the pond-oil since closure.

Estimates of average annual emission rates to air for hydrocarbons, chlorinated hydrocarbons and PCBs were obtained from the model for the operation period, 1973-1982. These are contained in Table 7.

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LITERATURE CITED

1. **Niedzielski, P. A.** (compiler), *Sludge Sampling Notebook*, Akin, Gump, Hauer and Feld, LLP, Washington, DC (August, 1992).
2. **Pisani, M. E.**, "Preliminary Remedial Investigation Report, Preprint," Combustion, Inc., Livingston Parish, Louisiana; Volumes 1 and 2; ERM-Southwest, Inc., Metairie, Louisiana (March, 1990).
3. **Bider, W. L., L. E. Seitter, and R. G. Hunt**, "Survey of the Oil Industry and Waste Oil Composition," Prepared for the U.S. EPA under Contract No. 68-02-3173, pp. 3-29 and 3-30 (April, 1983).
4. "Final Report Site Reconnaissance and Sampling Combustion, Inc. Site, Walker Louisiana," Dames and Moore, Job No. 25722-001-137 for Taylor, Porter, Brooks and Phillips, L.L.P., Baton Rouge, Louisiana (July, 1993).
5. **Rittmann, B. E.**, Chair, Committee on In-Situ Bioremediation, "In-Situ Bioremediation—When Does it Work?," National Academy Press, Washington, DC, p. 25 (1993).
6. **Eisenreich, S. J.**, "Sources and Fates of Aquatic Pollutants," *Advances in Chemistry*, Ch. 13, R. A. Hites and S. J. Eisenreich, eds., American Chemical Society, Washington, DC (1987).
7. **Guinasso, N. L., and D. R. Schink**, "Quantitative Estimates of Biological Mixing Rates in Abyssal Sediments," *J. Geophys. Res.*, **80**(21), 3032-3043 (1975).
8. "Site Investigation Follow-Up Report," Combustion Inc., Denham Springs, LA for Louisiana Department of Environmental Quality, Baton Rouge, prepared by Earth Technology Corp., Somerset, NJ (March, 1985).
9. **Thibodeaux, L.**, *Environmental Chemodynamics*, Chapter 4, 2nd Edition, John Wiley, NY (1996).
10. "Combustion, Inc. Expedited Removal Action, Livingston Parish, Louisiana," Woodward-Clyde, Monthly Progress Reports, WCC File 92B059C, Baton Rouge (July, 1993).
11. **Jones, R. K., J. Farr, D. Simecek-Beatty, K. Carney, D. Roques, C. Henry and E. Overton**, "The Evaporation of Benzene and a Series of Alkanes from Crude Oil," National Oceanic and Atm. Adm., Report No. HMRAD92-5 (August, 1992).
12. **Montgomery, J. H., and L. M. Wilkom**, *Groundwater Chemical Desk References*, Lewis Publishers, Chelsea, MI (1990).

Industrial Boiler Retrofit for NO_x Control: Combined Selective Noncatalytic Reduction and Selective Catalytic Reduction

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A 590 kW (2 MMBtu/hr), oil-fired, three-pass, fire-tube package boiler was retrofit with a combined selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR) system and demonstrated 85% nitrogen oxide (NO_x) reduction with less than 6 ppm ammonia slip. A urea-based SNCR solution was injected in the first pass, reducing NO_x and providing ammonia reagent for the SCR. A catalyst housing was designed to fit between the second and third passes, where the access doors of the boiler normally attach. The SCR catalyst volume of 0.04 m³ (1.5 ft³) provided a space velocity of 10,000 hr⁻¹ at a pressure drop of less than 1.5 cm (0.5 in) of water. Numerous runs demonstrated system repeatability and ease of operation. Continued tests using an on-line ammonia monitor, an on-line reagent flow meter, and a different fuel were conducted to show sustained performance and applicability.

INTRODUCTION

The 1990 Clean Air Act Amendments mandated reduced nitrogen oxide (NO_x) emissions for sources that have the potential to produce more than 22.7 metric tons (25 tons) of NO_x per year. Approximately 54,000 industrial, commercial, and institutional boilers currently in operation in the United States have been identified as sources that produce more than 25 tons of NO_x per year, presenting a need for low cost, high efficiency NO_x removal technologies [1].

For NO_x control technologies to be applied to existing boilers they must be easy to operate and must not impair the efficiency of the boiler. Some NO_x reduction technologies using combustion modifications include low NO_x burners with over-fire air (OFA), flue gas recirculation, and natural gas reburn which requires OFA in all cases. More common to retrofit situations are the post-combustion NO_x reduction technologies including selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR).

This work attempted to develop and demonstrate a combined SNCR/SCR system for retrofit application to an oil-fired package boiler. This type of SNCR/SCR system has been demonstrated on gas and coal systems at pilot [2] and full-scale levels. By combining SCR and SNCR a reduced catalyst size can be used which makes easier retrofits and reduces the pressure drop across the catalyst. The objective of the tests was to show that a typical package boiler can be effectively retrofitted, optimized, and operated without using excessive manpower and controls. Successful demonstration of this technology will define an option for the large population of existing NO_x control sources and will likely provide redesign parameters for new applications. For this industrial boiler application a catalyst housing was designed and added where the access doors of the boiler normally attach. A honeycomb-type ceramic catalyst with square cells was installed in the catalyst housing. The SNCR system consisted of a water-cooled, two-fluid reductant injector nozzle that removed a large fraction of the NO_x and supplied reductant to the downstream catalyst.

EXPERIMENTAL

The Boiler and Retrofit

The SNCR/SCR system was retrofitted to a 590 kW (2 MMBtu/hr), three-pass, North American package boiler capable of oil and/or gas firing (see Figure 1). The first pass was the main fire tube, while the second pass consisted of 24 6.4 cm (2.5 in) convective tubes, and the third pass consisted of 20 6.4 cm (2.5 in) convective tubes. The burner was a forced air burner located at the front of the boiler that used either No. 2 fuel oil or No. 2 diesel at an average rate of 53 L/hr (14 gal/hr) and 173 L/s (367 scfm) of air. Typical baseline operating concentrations for the No. 2 fuel oil were 109 ppm NO_x, 2.2% oxygen (O₂), 13.2 percent carbon dioxide (CO₂), 0 ppm carbon monoxide (CO), 0.6

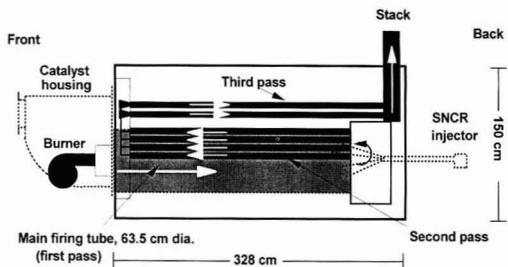


FIGURE 1 The North American package boiler side view with SNCR/SCR retrofit outlined by dotted lines.

ppm nitrous oxide (N_2O), and 174 ppm sulfur dioxide (SO_2). Generally, nitric oxide (NO) comprises more than 95% of the total NO_x , and NO was used for the NO_x numbers reported. The average gas flow estimated from the fuel consumption rate and the O_2 and CO_2 concentrations was 177 L/s (377 scfm), but a pitot tube velocity traverse 4 m (13 ft) downstream from the boiler measured 208 L/s (441 scfm); the difference is attributed to measurement error and in-leakage, the latter caused by use of an induced draft fan. The back of the boiler has an access plate that has a viewport, a thermocouple port, and a sampling/injection port, the latter centered axially on the 64 cm (25 in) diameter main fire tube. The SNCR reagent was injected countercurrent (toward the burner) through the sampling/injection port. Above and to the either side of the burner are access doors that expose the downstream ends of the second pass (first convective pass) tubes and the upstream ends of the third pass (second convective pass) tubes. The doors were removed, and the SCR catalyst housing was mounted where the doors had been located. A divider plate was installed to redirect the flow through the catalyst housing (Figure 2).

SAMPLING SYSTEM

The sampling system consisted of four sampling lines: a pre-catalyst residual ammonia (NH_{3RES}) sampling train, a post-catalyst NH_3 slip (NH_{3SLIP}) sampling train, an SO_2 sample line, and a sample line for the continuous emission monitors (CEMs). The CEM sample system drew a slipstream from the boiler and then pumped the sample to the CO_2 , CO, O_2 , and NO on-line analyzers as well as a gas chromatograph (GC) set up for N_2O measurement [3]. N_2O can be a byproduct of the SNCR NO_x reduction system [4]. N_2O is currently not regulated on the Federal level as an air toxic; however, it is a contributor to global warming

through the greenhouse effect [5]. The sample gas for the CEMs passed through a Hankinson chiller and was pumped through anhydrous calcium sulfate ($CaSO_4$) for removal of water subsequent to the chiller. The NH_3 measurement was acquired by pulling a slipstream of boiler gas through two 1 L impingers in series immersed in an ice bath. The first impinger contained 100 mL of 0.025 N sulfuric acid (H_2SO_4) solution that captured NH_3 , and the second impinger was dry and followed by a dry gas meter. The impinger rinse was measured by an ion selective electrode to obtain the NH_3 concentration. The ion selective electrode was calibrated using at least three standards before each set of samples were analyzed, and a spike made from a separate stock was used to check the calibration before and after each sample set was analyzed. Subsequent tests with the No. 2 diesel used a Bodneseework™ multi-component analyzer that provided water (H_2O), NH_3 , SO_2 , and CO_2 concentrations. Nominal baseline values for this fuel were 70 ppm NO_x , 12.5% CO_2 , 6.9 ppm SO_2 , 0.5 ppm CO, and 4.0% O_2 .

SNCR

The System

The SNCR injector, reagent dilution/delivery system, and the SNCR reagent itself were supplied by Nalco Fuel Tech (Naperville, Illinois). The SNCR system consisted of a metering pump and an air atomized reductant injector nozzle. The reagent was similar to $NO_xOUT A^{TM}$, a Nalco Fuel Tech product that consists of 50% urea (NH_2CONH_2), approximately 50% water, and small amounts of anti-scalants and dispersants [6]. Ammonia can also be used in place of urea, but its toxicity characteristics require additional safety permits and handling considerations. The water and urea-based reagent were pumped to a mixing chamber where the total injection liquid amounted to 0.19 L/min (3 gal/hr). The water/SNCR reagent mix was delivered to the injector where it was atomized with air. The normalized stoichiometric ratio (NSR) of reagent nitrogen (N) as NH_3 , to baseline N as NO_x , was controlled by varying the flowrate of SNCR reagent. NSRs from 0.5 to 4.5 were used with the No. 2 fuel oil. SNCR reagent feedrates were measured before and after every data set by pumping SNCR reagent from a burette instead of from the SNCR reagent reservoir barrel. The feedrates before and after the tests were consistent; however, the flow was not monitored during testing with the No. 2 fuel oil. The subsequent No. 2 diesel tests had an on-line reagent liquid flow meter, FLO-SENSOR™ Model 102-3TP, that provide accurate urea feed measurements, nominally 10 ml/min with maximum standard deviation of 0.34 ml/min; this corresponds to an NSR of 6.2.

Optimization

System optimization was affected by controlling the flow of the SNCR reagent which provided the reductant for the SCR. NH_3 , supplied by the breakdown of reagent NH_2CONH_2 , reduces NO_x in the presence of the catalyst at lower temperatures (approximately 230°C in our work). The objective when optimizing is to find the injection condition where SNCR removal is most efficient while ensuring that there is sufficient SNCR reagent to supply enough residual NH_3 (NH_{3RES}) for the catalyst to remove the residual, post-SNCR NO_x (NO_{XRES}). The ratio of these two val-

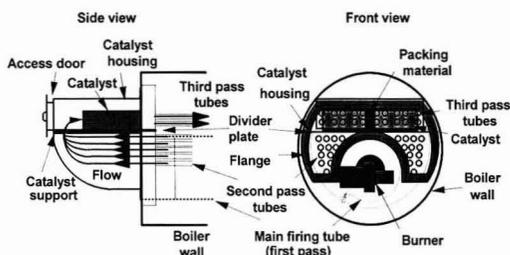


FIGURE 2 SCR retrofit diagram.

ues, NH_{3RES}/NO_{XRES} , defines the pre-catalyst stoichiometric ratio (SR_{RES}). Preliminary tests varied the amount of air, the injector insertion distance into the boiler, the type of nozzle at the tip of the injector, and the total flow of water at a fixed NSR. Although NO_x removal was greater at higher water flowrates, the flow was kept fixed at 0.19 L/min (3 gal/hr) to maintain sufficient boiler efficiency. The temperature profiles acquired before the retrofit indicated that the optimum SNCR injection temperature was close to the end of the main fire tube, but when the SNCR reagent solution and carrier gas were injected they introduced temperature gradients in the main fire tube that resulted in unexpected temperature profile results. The temperature profiles with the SNCR injection indicated that the temperature at the end of the main fire tube was much lower (680°C) than optimum (about 900°C) [7]. This can be attributed to the liquid from the SNCR reagent injection adhering to and then evaporating from the surface of the thermocouple, yielding a thermocouple temperature measurement that is lower than the actual gas temperature. The optimum injector insertion distance for all nozzles, determined by the SNCR NO_x reduction (X_{SNCR}), was between 0 and 20.3 cm (8 in) from the back end of the boiler.

Six different nozzles were tested: three nozzles had round-orifice diameters of 0.1 (0.0388), 0.2 (0.0775), and 0.4 cm (0.155 in) that provided a cone spray pattern; one nozzle had six 0.18 cm (0.07 in) holes evenly distributed 0.28 cm (0.11 in) from the center of the nozzle that provided a cloud spray pattern; one nozzle had an oval orifice that created a fan spray pattern; and one had an oval orifice at a 45° angle to provide an angled fan spray pattern. In the No. 2 fuel oil tests, both fan spray nozzles performed better than the cloud spray, which, in turn, performed better than the cone spray nozzles. The optimum settings for air pressure and injector distance from the end of the boiler were different for all the nozzles except the two fan spray nozzles. The angled fan spray with the angle pointing up was determined to be the best nozzle to use. The removal was greatest with the injector tip 3.8 cm (1.5 in) from the end of the boiler, and the air at 241 kPag (35 psig). The factors that went into determining the best nozzle were the combined SNCR and SCR total NO_x reduction (X_{TOT}), NH_{3SLIP} , and N_2O emissions. Droplet tube-impingement should also be considered in applications; boiler- and nozzle-specific flow modelling will determine these potential impacts.

The No. 2 diesel tests worked best with the fan spray nozzle inserted 76.2 cm (30 in) into the boiler where the temperature was measured to be 650°C.

SCR

The SCR catalyst was a commercially available titanium and vanadium ceramic catalyst with 7.6 square cells/cm² operating at a nominal level of 10,000 h⁻¹ space velocity [standard temperature and pressure (STP)]. The catalyst did not appear to degrade over about 280 hours of operation; it also did not collect soot despite overnight shutdown and morning re-start for each test with No. 2 fuel oil, which could cause temperature changes and increase sooting during startup. Sometimes NH_3 can combine with sulfur trioxide (SO_3) to form sticky ammonium hydrogen sulfate [(NH_4)HSO₄], or ammonium bisulfate salt deposits that can cause tube plugging and fouling. Catalysts can contribute

to this formation by converting SO_2 to SO_3 . The catalyst had no effect on SO_2 or N_2O , and no NH_3 -based salts were evident in the boiler. The pressure drop across the catalyst was measured by a manometer and by a Magnahelic™ pressure gauge to be nominally 1 cm (0.4 in) of water. Long-term operation is necessary to determine catalyst durability and potential tube deposit impacts.

Boiler Operation

The boiler was always operated at full load. It was started and run for 3 h with just water and air injected through the injector to establish temperature, NH_3 , and NO_x equilibrium. Then the baseline (no reagent) readings were taken and it was run for 3 h more with the SNCR reagent flowing. After 3 h equilibration time, NH_{3RES} , NH_{3SLIP} , and CEM measurements/samples were recorded. The system was allowed 1 h to return to equilibrium, and then post-test baseline readings were taken.

The No. 2 diesel tests consisted of constant sampling for 2 days. Some downtime was caused by burner adjustments and CEM maintenance. The data divided into "run" times that are indicative of only the time when the boiler was in equilibrium and the monitoring systems were operating properly.

RESULTS AND DISCUSSION

The SNCR system typically removed 30 to 40% of the NO_x . Figure 3 shows X_{SNCR} and the resultant SR_{RES} for varying NSR values. The data points are all using the angled fan spray nozzle with the nozzle tip located 1.5 in from the back wall of the boiler. Variation of NSR from 1 to 4 shows little effect on X_{SNCR} (filled points) and no consistent trend for SR_{RES} (open points).

The SCR NO_x removal performance versus SR_{RES} is shown in Figure 4. The catalyst shows consistent NO_x reduction (X_{SCR}) trends with increasing SR_{RES} until SR_{RES} reaches values above approximately 0.7, where X_{SCR} levels off at about 80%. This is a fairly typical trend for a catalyst performance. The points on Figure 4 are from the angled fan spray nozzle.

The ratio of the decrease in NO_x to the decrease in NH_3 averaged 1.33 across the catalyst. The stoichiometry of the

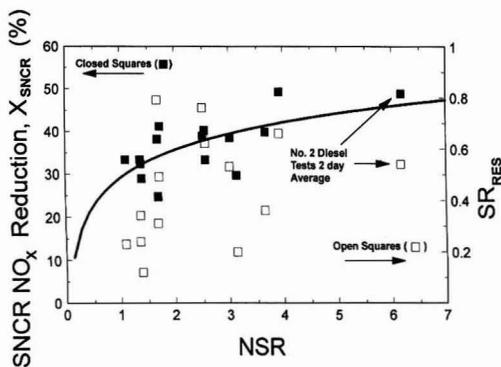


FIGURE 3 SNCR system performance. Angled fan spray nozzle with injector tip 1.5 in from the back of the boiler.

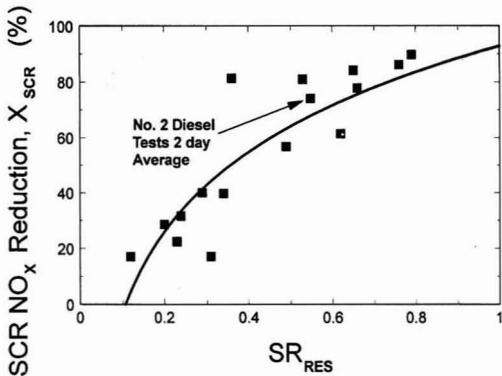


FIGURE 4 NO_x reduction across catalyst for varying SR. NH₃ is between 10 and 55 ppm.

reaction should result in a ratio of 1. NH₃ measurements that are too low (due to NH₃ breaking through the impingers, or due to dry gas meter calibrations returning sample volumes that are higher than actual) could cause the ratio to seem higher than 1.

The wide range of testing conditions reported did not result in an obvious relationship of NSR to X_{SNCR} or SR_{RES} (Figure 3). Nonetheless, the optimal SR_{RES} (> 0.7, from Figure 4) is probably obtained at NSR values around 2 or higher. This is more clear from Figure 5, which shows the system's total NO_x removal, X_{TOT}, versus NSR. This shows that under optimal conditions this retrofit established NO_x reduction of 93%. All ammonia slips with No. 2 fuel oil were less than 6 ppm, so there is clearly enough catalyst to remove the residual NH₃ from the SNCR process.

N₂O formation increases with increasing NSR values (Figure 6). Under fairly typical operating conditions of NSR = 2, measured N₂O emissions are about 10 ppm. These values have not been accounted for in prior NO_x reduction percentages.

The sometimes large degree of scatter in the data is indicative of the varied SNCR chemical injection rates during the No. 2 fuel oil tests. Practical operation of an SNCR/SCR system would involve finding the optimum conditions for each specific boiler and operating within those conditions. Shakedown, optimization, and long-term operation

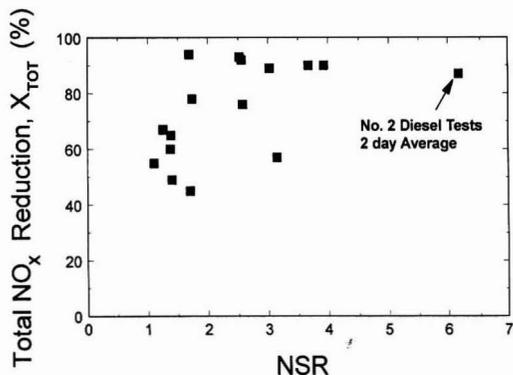


FIGURE 5 NO_x reduction for varying NSR. Angled fan spray nozzle data only.

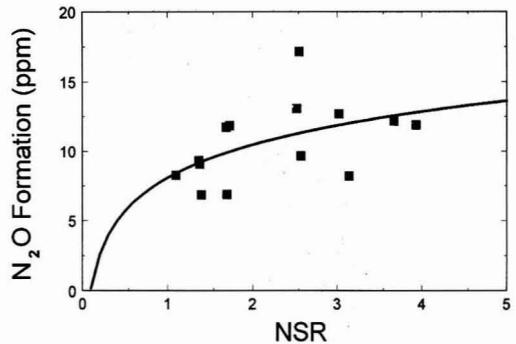


FIGURE 6 N₂O formation across catalyst for varying NSR.

of this system are ideally suited for a neural network feedback/control in the case where load-following, predictive capabilities are desired or a fuzzy logic control system in simpler/easier applications.

The subsequent No. 2 diesel tests were included to demonstrate optimized, steady-state operating performance. The run times varied in length from 42 minutes to 7 hours with a total test time of 14.5 h. The test periods were separated by periods where the burner or the sampling system was being adjusted. The catalyst temperature for these tests was nominally 233°C but did get as high as 300°C. This variation did not seem to affect the catalyst performance. For a baseline NO_x level of 70 ppm, X_{SNCR} was consistently 50% for the entire test period while X_{SCR} was 73%. The X_{TOT} was between 83 and 89% with an average of 87%. NH_{3SLIP} concentration for these subsequent runs was between 11 and 6.7 ppm with an average of 9.3 ppm.

CONCLUSION

An SNCR/SCR hybrid system retrofit to a fuel-oil-fired package boiler had an apparent optimum NSR around 2 where 85% NO_x reduction could be achieved without exceeding 6 ppm NH_{3SLIP}. N₂O formation was generally below 15 ppm. At the optimum NSR, it was nominally 10 ppm.

Use of No. 2 diesel fuel and constant operation for 40 h showed that the retrofit hybrid system could reduce NO_x by 87% while keeping NH_{3SLIP} below 11 ppm during constant operation.

The SNCR/SCR hybrid system was easily retrofit to our existing oil-fired package boiler. Although the design of the SCR catalyst housing was specific to this boiler, similar designs could be developed for other units. Equipping new boilers via minor design changes would probably be even easier and more effective than retrofitting old ones. Once the system is installed, optimization time may be about 1 or 2 days. Changes in temperature profiles may make optimization difficult. Current work is developing a neural network and fuzzy logic control system to counter this.

Further testing may be needed to assess long term boiler effects and long term catalyst durability to determine added costs from reagent use and catalyst replacement.

ACKNOWLEDGMENTS

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tion of the SNCR injector, reagent, and reagent delivery system. Special thanks to John E. Hofmann and M. Linda Lin (Nalco Fuel Tech) for technical advice.

NOTATION

NH_{3RES} = The residual ammonia in the boiler after the SNCR reaction measured before the catalyst.

NH_{3SLIP} = The residual ammonia in the boiler measured after the catalyst.

NSR = The normalized stoichiometric ratio of input nitrogen (from the SNCR reagent) to the nitrogen in the boiler in the form of NO_x .

NO_{XRES} = The residual NO_x in the boiler after the SNCR reaction measured before the catalyst.

SCR = Selective catalytic reduction.

SNCR = Selective noncatalytic reduction.

SR_{RES} = The stoichiometric ratio of the post-SNCR residual reagent nitrogen, NH_{3RES} , to post-SNCR residual nitrogen measured before the catalyst, NO_{XRES} .

X_{SCR} = The percent reduction of NO_x across the catalyst.

X_{SNCR} = The percent reduction of NO_x from the baseline level to the NO_x level measured after the SNCR reaction before the catalyst.

X_{TOT} = The percent reduction of NO_x from the baseline to the NO_x level measured after the catalyst.

LITERATURE CITED

1. **U.S. Environmental Protection Agency**, Alternative Control Techniques Document— NO_x Emissions from

Industrial/Commercial/Institutional (ICI) Boilers, Office of Air and Radiation, Office of Air Quality Planning and Standards, Research Triangle Park, NC, EPA-453/R-94-022, NTIS PB94-177177, (March 1994).

2. **Gullett, B. K., et al.**, "NO_x Removal with Combined Selective Catalytic Reduction and Selective Noncatalytic Reduction: Pilot-Scale Test Results," *J. Air & Waste Manage. Assoc.*, **44**, pp. 1188-1194 (1994).
3. **Ryan, J. V., and S. A. Karns**, "On-line Monitoring of Nitrous Oxide From Combustion Sources Using an Automated Gas Chromatograph System," In: Proceedings: 1992 U.S. EPA/A & WMA International Symposium, Measurement of Toxic and Related Air Pollutants, Durham, NC, U.S. Environmental Protection Agency, EPA/600/R-92/131, (1992).
4. **Muzio, L. J., et al.**, "N₂O Formation in Selective Non-Catalytic NO_x Reduction Processes," In: Proceedings: 1991 Joint Symposium on Stationary Combustion NO_x Control, Washington, DC, Vol. 2, U.S. Environmental Protection Agency, EPA-600/R-92-093b, NTIS PB93-212850, (1992).
5. **Kramlich, J. C., and W. P. Linak**, "Nitrous Oxide Behavior in the Atmosphere, and in Combustion and Industrial Systems," *Prog. Energy Combust. Sci.*, **20**, pp. 149-202 (1994).
6. **Lin, M. L., and D. V. Diep**, "NO_xOUT PLUS—An Improved SNCR Process for NO_x Emission Control," presented at AIChE Annual Meeting, Miami Beach, FL (1992).
7. **Teixeira, D. P., et al.**, "Widening the Urea Temperature Window," In: Proceedings: 1991 Joint Symposium on Stationary Combustion NO_x Control, Washington, DC, Vol. 3, U.S. Environmental Protection Agency, EPA-600/R-92-093c, NTIS PB93-212868, (1992).

Whole Effluent Toxicity Reduction by Ozone

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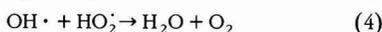
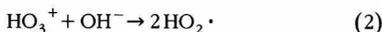
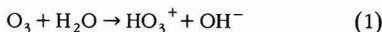
Parametrix, Inc., 1231 Fryar Avenue, Sumner, WA 98390

An investigation of the effects of ozone and ozone-induced hydroxyl radical on reducing whole effluent toxicity is discussed relative to the application of ozone for industrial water treatment. Results from operation of an ozone system treating industrial effluent from a lead/zinc mine in Colorado are presented. The mine discharges 1,000 gpm (227 m³/hr) of wastewater and has historically exceeded Whole Effluent Toxicity (WET) limits. On occasion, it has exceeded numeric limits for copper, ammonia, and cyanide.

Based on test results, an applied ozone to COD ratio of 3:1 by weight and a contact time of 30 minutes was found to be effective for reducing whole effluent toxicity at pH 11 but not at pH 7, indicating oxidation by hydroxyl radical to be the dominant mechanism responsible for toxicity reduction. At an applied ozone to COD ratio of 3:1 and a pH of 11, toxicity was reduced with survival increasing improved from 0 percent survival to 100 percent survival for *Ceriodaphnia dubia* and fathead minnow (*Pimephales promelas*) based on 48-hour and 96-hour WET tests, respectively. This application rate of ozone with a 99 percent mass transfer efficiency was also effective in reducing total cyanide from an average of 0.45 mg/L to less than 0.05 mg/L and COD from 28 mg/L to 9 mg/L. The rate of ammonium nitrogen oxidation appeared to follow first-order kinetics; however, the rate of oxidation was decreased significantly by the presence of COD.

INTRODUCTION

The reactions of ozone (O₃) in wastewater can be divided into two types: direct ozonation reactions and free radical decomposition reactions. In pure aqueous solution, ozone is thought to decompose as follows [1]:



The direct reactions of ozone involving molecular O₃ are highly selective and relatively slow compared with reactions involving free hydroxyl radicals (OH·). The hydroxyl radical typically reacts a million to a billion times faster than ozone. Hydroxyl radicals have much higher oxidation potential and are also much less selective in their reaction than ozone itself. The free radical produced by decomposition of ozone is considered to be the principal

reacting species involved in the destruction of organic toxicants [1, 3, 4].

Advanced oxidation processes (AOPs) involve acceleration of O₃ free radical decomposition, thereby increasing the OH· concentration and promoting oxidation of toxic organics. Several AOPs that work in combination with ozone to promote hydroxyl radical formation include hydrogen peroxide, UV light, and high pH. In addition to accelerating ozone decomposition, high pH ozone (pH 9 and greater) is favorable for ammonia oxidation, cyanide destruction, and precipitation of heavy metals [5].

This paper focuses on using high pH in combination with ozone to remove the compounds of interest as described in the following case study.

CASE STUDY

Background

In November 1994, an ozone treatment system was installed to treat wastewater effluent from an active lead and zinc mine in Colorado. The mine discharges, on average 1,000 gpm (227 m³/hr) of wastewater into a tributary of the Arkansas River. Ozone was selected for wastewater treatment because of its potential ability to destroy toxic organics, precipitate heavy metals and metal complexes, destroy cyanide, and oxidize ammonia. Thus, potentially all treatment objectives for the site could be satisfied by one simple treatment system. The chemicals of concern and associated numeric discharge requirements are shown in Table 1.

In addition to meeting these numeric standards, the facility is required to meet Whole Effluent Toxicity (WET) test limits. The treatment objective for toxicity is to obtain no statistically significant effects in 100 percent effluent for *Ceriodaphnia dubia* and fathead minnows (*Pimephales promelas*). Based on a Toxicity Identification Evaluation

TABLE 1. Chemicals of Concern and Numeric Standards

Chemical	Effluent Range (mg/L) ⁽¹⁾	Effluent Limit (mg/L) ⁽²⁾
Ammonia	2-7	4.5
Copper	0.025-0.5	0.05
Cyanide	0.2-0.5	0.1

⁽¹⁾Typical effluent range without ozone treatment.

⁽²⁾Effluent limit based on 30-day average concentration.

TABLE 2. Mine-Mill Reagents Contributing to Effluent Toxicity

Reagent	LC50 (mg/L)	Estimated Usage (mg/L)	TUs ⁽¹⁾
Sodium Isopropyl Xanthate	0.9	7.1	7.9
Potassium Amyl Xanthate	2.4	2.1	0.88
Sulfhydryl Compounds	15.5	7.5	0.48

⁽¹⁾TUs = Toxic Units (the usage rate ÷ the LC50)

(TIE) conducted on the effluent, organic mine-mill reagents were determined to contribute significantly to effluent toxicity. Effluent Toxicity Units (TUs) for the primary reagents of concern are shown in Table 2. A TU value of greater than 1 represents significant toxicity.

In the mill, finely ground ore is concentrated in a froth flotation circuit. Thickener overflow and tailings waste streams containing residual organic reagents and heavy metals are adjusted to pH 10.5 to 11 and discharged to a large settling pond (tailings pond). In the tailings pond, metals are precipitated and settled at high pH. The decant from the pond is routed through sand filters before final discharge.

Description of Treatment System

As shown in Figure 1, the ozone treatment system was installed directly downstream of the existing tailings pond and sand filter, and an additional filter was installed after the ozone system to remove metals oxidized by ozone.

Ozone is generated on-site using pure oxygen stored in a 13,000 gallon (49 m³) pressurized tank. Each of the two ozone generators (Hankin Ozotec II) is rated at 300 pounds (136 kg) O₃ per day at 4 percent concentration. Filtered wastewater flows by gravity through three stainless steel contactors connected in series. Each contactor has a diameter of 12 feet (3.7 m) and a height of 20 feet (6.1m). Ozone

is fed to each contactor through 8-inch (20 cm) stainless steel venturi injectors, and wastewater from the contactors is recirculated through each injector at a rate of 2,000 gpm (454 m³/hr).

The injection/recirculation contact system provides very high ozone transfer efficiencies, on the order of 99 percent. This compares favorably with other conventional methods of contacting ozone such as mixed tank reactors and fine bubble diffusers, which provide transfer efficiencies on the order of 90 percent [1, 2].

Because the wastewater is weakly buffered, ozonation results in a drop in pH. To maintain pH between 10.5 and 11, sodium hydroxide is automatically added to the contactors. The ozone feed rate may be adjusted manually or automatically based on wastewater flow or ozone off-gas concentrations. Off-gas ozone is routed through an ozone destruction unit prior to atmospheric discharge.

Removal of Toxicity

Figure 2 shows test results for COD and toxicity during ozonation of wastewater at high pH. Ozone was applied at varying doses ranging from 1:1 to 3:1 (mg/L O₃:mg/L initial COD). The initial COD value was 28 mg/L. In this case, because the transfer efficiencies are high (greater than 90 percent), the applied ozone dose is approximately equal to the absorbed ozone dose. As shown in Figure 2, ozone at an applied dose of 84 mg/L (O₃:COD = 3:1), reduced toxicity to meet the treatment objective and reduced COD by greater than 60 percent.

It was found that ozone treatment resulted in a drop in pH from 11 to 9. The observed drop is expected due to consumption of hydroxide ion. Also, it is typical for ozone to form carboxylic acids during the oxidation of organics, leading to pH depression. To control pH at 11, sodium hydroxide solution was added to the contactors.

Effect of pH on Ozone Performance

To observe the effects of pH on ozone treatment, tests were conducted on wastewater at both high pH (11) and

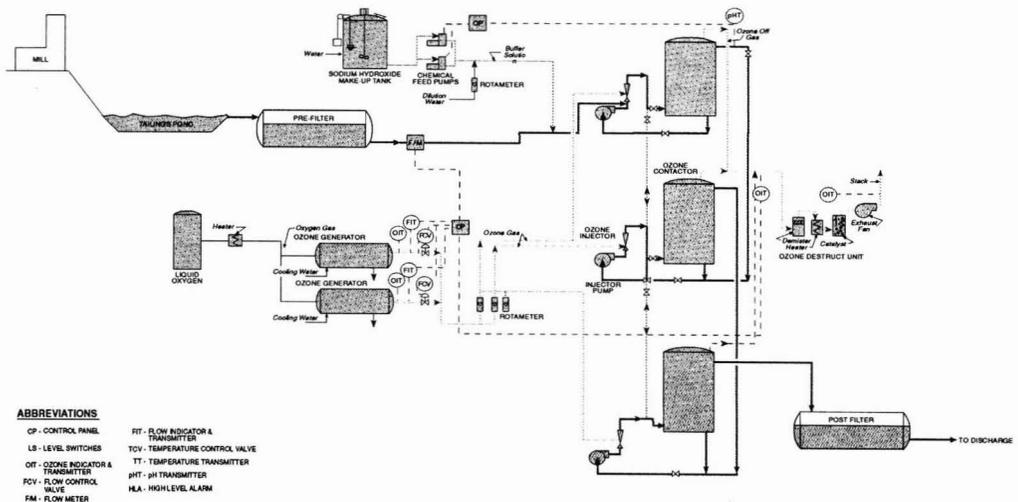


FIGURE 1 Ozone treatment system.

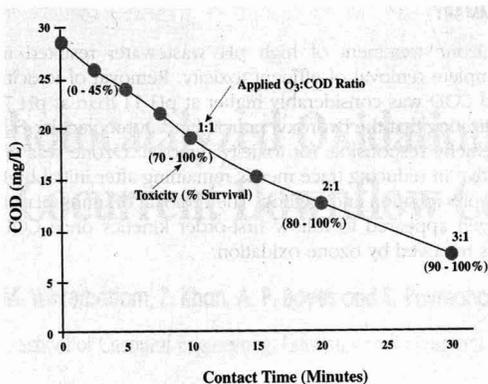


FIGURE 2 Toxicity and COD reduction by ozone at high pH.

neutral pH (7). Both tests involved ozone addition at a 2:1 ratio of O₃ to COD and a long contact time of 100 minutes. Figure 3 shows a direct comparison between treatment performance at high pH versus treatment at neutral pH. As shown, toxicity is completely eliminated by ozone at high pH, but no toxicity reduction is observed at neutral pH. These findings indicate that oxidation by hydroxyl radical is primarily responsible for removal of organic toxicity. Figure 3 also shows that reduction in COD and cyanide is considerably greater at high pH as compared to ozone at neutral pH.

Oxidation of Cyanide

Ozone reacts rapidly with free cyanide ion and many stable metal cyanide complexes [5]. Ozonation of cyanide proceeds rapidly to form cyanate as shown by the following reaction:



The oxidative/hydrolytic destruction of cyanate ion proceeds much more slowly upon continued treatment with ozone:

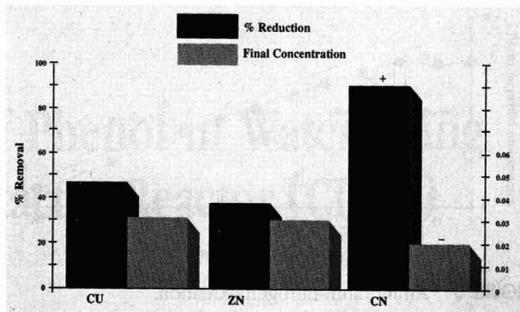
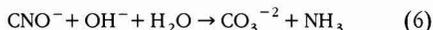


FIGURE 4 Removal of cyanide and heavy metals by ozone.

This study shows that cyanide can be removed to below 0.05 mg/L by an applied ozone dose of 30 mg/L (O₃:COD = 1:1) and a 15-minute contact time. As shown in Figure 4, the percentage reduction in cyanide by ozone is greater than 90 percent. Cyanide removal was only 18 percent at neutral pH, supporting research literature indicating that cyanide reactions are faster at high pH [5].

Reduction of Heavy Metals

All easily oxidized heavy metals can be oxidized by ozone. Specific heavy metals that have been oxidized under wastewater treatment conditions include arsenic, aluminum, lead, nickel, chromium, copper, cobalt, barium, zinc, cadmium, and organic complexes of some of these metals [5]. Netzer and Bowers [6] showed that a large percentage of these metals is removed by lime adjustment to alkaline conditions and that the remaining dissolved metals are precipitated by ozone. Combined treatment with lime followed by ozone resulted in greater than 99.5 percent removal of aluminum, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, and zinc [6].

As shown in Figure 1, the treatment system is arranged to provide pre- and post-ozone filtration. The first filter removes precipitated metals and other suspended solids that carry over from the tailings pond. Suspended solids exhibit an appreciable ozone demand, and therefore pre-filtration is necessary to conserve ozone. The second filter in the treatment system is located to remove trace dissolved metals or complexed metals that are oxidized by ozone. Both the pre-filter and post-filter contain the same sand media.

The average removal of copper and zinc by ozone and post-filtration is shown in Figure 4. The results are based on an ozone to COD ratio of 2:1 and a contact time of 100 minutes. Both copper and zinc were removed to near detection limits (0.025 and 0.02 mg/L, respectively) and well below discharge standards. Both metals were already at low levels before treatment, approximately 0.05 mg/L.

Removal of the trace metals may be associated with oxidation or possibly by destruction of metal-cyanide complexes. In either case, ozone is shown to be effective in reducing trace metals remaining after initial high pH precipitation and filtration.

Oxidation of Ammonia

Under the proper conditions, ammonia may be oxidized completely to nitrate by ozone in accordance with the following stoichiometry:

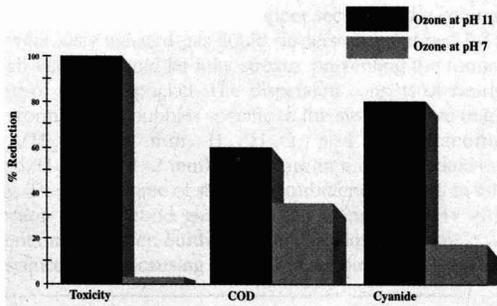


FIGURE 3 Comparison of ozone at high pH vs. low pH.

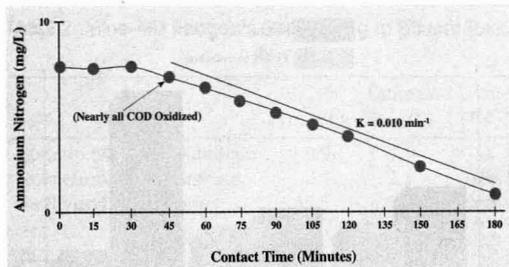


FIGURE 5 Ammonium-nitrogen oxidation.



The oxidation reaction is first order with respect to the concentration of ammonia, and reaction kinetics are greatly accelerated at high pH [7]. For example, the oxidation of ammonia is about 10 to 20 times faster at pH 9 than at pH 7, and the molar ratio of ozone consumed to ammonia oxidized is about 8 times higher at pH 7 than at pH 9 [7]. The fact that ammonia oxidation is faster at high pH indicates that the hydroxyl radical may be driving the reaction.

The ozone contactors were operated in batch mode to evaluate the removal of ammonium nitrogen with respect to time. The contactors were fed with ozone at a continuous rate of 1 mg/L per minute. The results are displayed on a semi-log graph in Figure 5. As shown, the rate of ammonia oxidation accelerates considerably once most of the COD has been removed. In this case, the treatment objective for ammonia of 4.5 mg/L was met at an accumulative ozone dose of 75 mg/L and a contact time of 75 minutes. The rate of oxidation appears to be first order in ammonia, as illustrated by the straight line in Figure 5. The first-order rate constant is calculated to be 0.01 min^{-1} .

SUMMARY

Ozone treatment of high pH wastewater resulted in complete removal of effluent toxicity. Removal of toxicity and COD was considerably higher at pH 11 than at pH 7, indicating that the hydroxyl radical (and not molecular O_3) is chiefly responsible for toxicity removal. Ozone was effective in reducing trace metals remaining after initial high pH precipitation and settling. The removal of ammonia nitrogen appeared to follow first-order kinetics once COD was removed by ozone oxidation.

LITERATURE CITED

1. **White, Clifford**, *The Handbook of Chlorination*, 2nd ed., Van Nostrand Reinhold Company, NY (1986).
2. **Lin, H. L., and K. L. Yeh**, "Looking to Treat Wastewater? Try Ozone," *Chemical Engineering* (May, 1993).
3. **Glaze, W. H., and J. W. Kang**, "Advanced Oxidation Processes for Treating Groundwater Contaminated with TCE and PCE," *JAWWA* (May, 1988).
4. **Plant, L., and M. Jeff**, "Hydrogen Peroxide: A Potential Force to Destroy Organics in Wastewater," *Chemical Engineering* (Sept., 1994).
5. **Rice, R. G., and M. E. Browning**, *Ozone Treatment of Industrial Wastewater*, Noyes Data Corporation, NJ (1981).
6. **Netzer, A., and A. Bowers**, "Removal of Trace Metals from Wastewater by Lime and Ozonation," in *Proc. First Intl. Symp. on Ozone for Water and Wastewater Treatment* (1975).
7. **Singer, P. C., and W. B. Zilli**, "Ozonation of Ammonia in Wastewater," *Water Research*, Vol. 9 (1975).

Photocatalyzed Oxidation of Phenol in Water Using a Cocurrent Downflow Contactor Reactor (CDCR)

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The oxidation of aqueous solutions of phenol as a typical model pollutant has been carried out in the presence of an ultra-violet (UV) irradiated TiO₂ catalyst in a CDC reactor. The CDCR was fitted with internally mounted 30 W and 1.0 kW UV lamps. The reactions were carried out at 40–50 °C and 202.6 kPa, with the reactor being operated in closed loop recycle mode and suspended catalyst being recirculated. The CDCR is a device of high mass transfer efficiency, giving unusually large gas hold-up (approximately 50%). The CDCR was operated (i) with oxygen mass transfer and dissolution in the zone above the UV source and (ii) with oxygen dispersion and mass transfer occurring along and around the lamp housing. Using the higher powered lamp, 100% conversion of phenol was obtained from solutions containing 100 mg/dm³. Under specific conditions the presence of TiO₂ catalysts was observed to give the most rapid oxidation degradation of the phenol.

In today's environment with increasingly stringent national and international regulations regarding wastewater treatment, the requirement to develop innovative and more efficient wastewater technologies has never been so great. These technologies are not only required to decompose toxic industrial wastewater effluents to innocuous products, but also aim to improve water quality. One such technology to improve wastewater degradation makes use of the Cocurrent Downflow Contactor Reactor (CDCR), (Boyes et al. [1]).

The CDCR is a mass transfer efficient gas-liquid contacting device, where the gas and liquid stream are introduced cocurrently through an orifice and entry zone at the top of a fully flooded column. In the upper section of the column a vigorously agitated gas-liquid dispersion is formed by a high velocity liquid jet inlet stream, preventing the formation of any gas pocket. The dispersion consists of nearly uniformly sized bubbles specific to the system in use (e.g., O₂/H₂O, 4–5 mm; H₂/H₂O, 3–4 mm; Itaconic acid/H₂/H₂O, 1–2 mm), which are in a close packed array. The high degree of shear and turbulence created in this section causes good gas-liquid contacting and very efficient mass transfer. Further down the column, bubble coalescence occurs causing slightly larger bubbles to rise up

the column which are broken up by the incoming high velocity inlet stream.

Some of the advantages available with the CDCR over more conventional devices are (Boyes et al. [1]).

- Lower power consumption,
- Smaller containment volume (no entrainment),
- Easy scale-up without any loss in mass transfer efficiency,
- 100% gas utilization and 97% approach to equilibrium in short times,
- Control of bubble interfacial area (1000–6000 m²/m³ depending on bubble size),
- No moving parts—inherently reliable,
- High gas holdup (0.5–0.6),
- Tolerance to particles and therefore suitable for slurry chemical reactions.

To indicate the high degree of gas-liquid mass transfer achieved in the CDCR, typical values of $k_L a$ (the volumetric gas-liquid mass transfer coefficient) for O₂/H₂O systems are found in the range 0.25–1.5 s⁻¹ and are greater than $k_L a$ values given for more conventional bubble column reactors for the same reaction system.

The use of advanced oxidation processes (AOPs) such as photocatalysis and oxidation to treat aqueous organic pollutants has been a subject of considerable interest over the past 10–15 years (Herrmann et al. [2]; Serpone et al. [3]; Augugliero et al. [4]; Okamoto et al. [5]; Bard [6]). The governing principle of AOPs is the formation of hydroxyl radicals (HO·) which are considered to be the principle oxidizing species for aqueous organic compounds, producing an oxidizing power beyond that achievable using single chemical oxidants such as chlorine, hydrogen peroxide and ozone (Serpone et al. [3]; Okamoto et al. [5]; Sharratt [7]). The oxidizing potential of a species is a measure of its oxidizing strength and for hydroxyl radicals is exceptionally high at 2.8 eV. Oxidizing potentials of various species are given in Table 1 (Cotton & Wilkinson [8], Sharratt [7]).

With the exception of perfluorinated materials, the hydroxyl radical will react with almost all organic compounds. Many different techniques can be employed to generate hydroxyl radicals with all methods involving the use of an oxidant (H₂O₂, O₃, O₂) together with an activating system (UV light, catalyst, alkali or other oxidizing species). One example of an AOP is photocatalysis.

The concept of photocatalysis is the activation of a photocatalytic semiconductor, such as TiO₂ by radiation of a

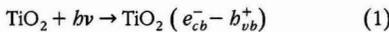
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TABLE 1. Oxidation Potentials of Various Species

Species	Oxidation Potential eV
Hydroxyl Radical	2.80
Ozone	2.07
Hydrogen Peroxide	1.77
Permanganate ion	1.67
Chlorine dioxide	1.50
Chlorine	1.36
Oxygen	1.23

suitable wavelength and energy ($h\nu$) to promote excitation of electrons, which are accepted by oxygen on the semiconductor surface yielding unstable superoxide radical ions ($O_2^{\cdot-}$) and further yielding hydroxyl radicals $HO\cdot$.

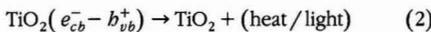
The principles governing the photocatalytic oxidation of organic species on a semiconductor material (i.e., TiO_2) are given in detail in Figure 1. The following reaction scheme can be proposed for the irradiation of a photocatalyst by light (i.e., UV) inducing a separation between the electrons (e^-) and holes (h^+) in the valence bond (vb) and migration of electrons to the conduction band (cb), i.e., for TiO_2 .



where

e_{cb}^- = denotes conduction in band electrons,
 h_{vb}^+ = denotes valence band holes.

If there are no electron and holetraps (acceptors) available at the surface of the particle, recombination between electrons and holes can occur with the liberation of heat and light.



The chief electron acceptor is adsorbed O_2 on the semiconductor surface which yields an unstable superoxide radical ion $O_2^{\cdot-}$.



The superoxide radical ion may react subsequently with

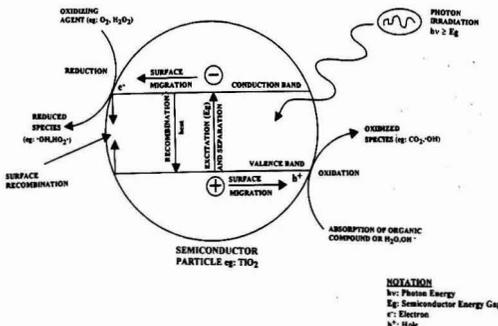
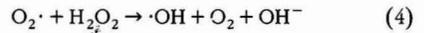
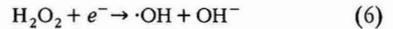
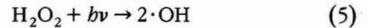


FIGURE 1 Simplified illustration of the reactions occurring on a semi-conductor photocatalyst for the oxidation of aqueous organic pollutants.

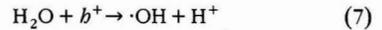
surface generated or added H_2O_2 to form hydroxyl radicals $HO\cdot$.



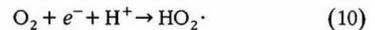
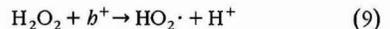
Alternatively $HO\cdot$ can be produced by the reaction of H_2O_2 in any of the following schemes;



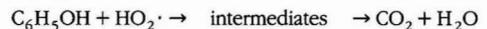
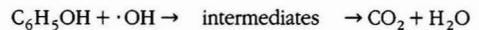
Simultaneously, the photogenerated holes h^+ may combine with adsorbed H_2O or hydroxide anions OH^- on the photocatalyst surface to yield hydroxyl radicals;



In addition, H_2O_2 can react with holes h^+ , or simultaneously O_2 with electrons e^- to form a hydroperoxide radical $HO_2\cdot$ which in turn acts as a strong oxidizing intermediate for organic compounds.



Taking into account all possible reactions, general reaction schemes for heterogeneous photocatalytic oxidation of aqueous organic pollutants (i.e., phenol) can be shown as;



OBJECTIVES

The primary objectives of this study were to investigate the behavior of the cocurrent downflow contactor reactor (CDCR) for the photocatalytic oxidation of aqueous solutions of phenol as a typical model pollutant. Many factors influence the photocatalysis process and some of the major factors were identified and further investigated. Some of these factors include;

- (i) Operating conditions of the CDCR,
- (ii) The effects of solution pH,
- (iii) The effects of catalyst loading,
- (iv) Nature of reaction products.

EXPERIMENTAL

All reactions were carried out in a glass CDC reactor constructed from standard QVF glass fittings. The basic outline of the photocatalytic CDC reactor in schematic form is shown in Figure 2. The photocatalytic CDC reactor consists essentially of two regions: (i) A top section for absorption only and (ii) a bottom reaction section which allows gas-liquid absorption with simultaneous chemical reaction. The bottom section housed the UV lamps which were encased in a quartz sheath. The UV lamps used were of different lengths (i.e., 30 W lamp, 1.0 m; 1.0 kW lamp, 0.5 m) and the reaction section was designed based on the length of lamp giving different system and reactor volumes.

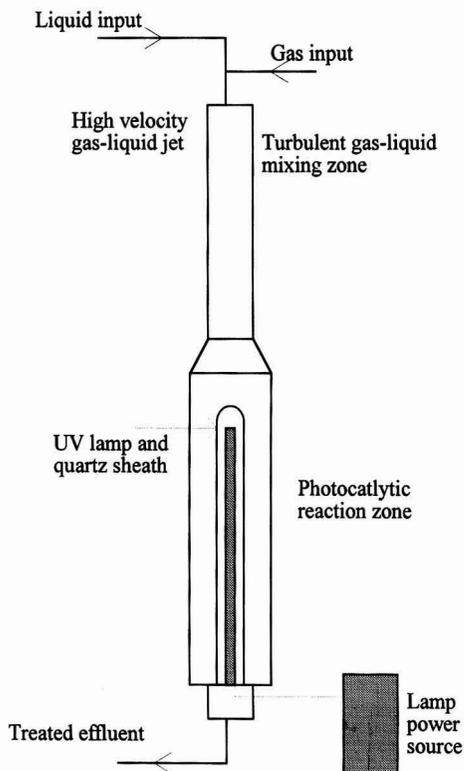


FIGURE 2 Schematic diagram of CDC reactor.

The CDC operating conditions used:

	Reactor A	Reactor B
Total system volume	1.80 dm ³	10.0 dm ³
Reactor volume	6.2 dm ³	3.0 dm ³
Reaction pressure	202.6 kPa	202.6 kPa
Reaction temperature	40–50 °C	40–50 °C
UV Lamp used	30 W @ 254 nm	1000 W @ 254 nm

The CDC reactor was operated in batch mode with total recycle.

Phenol was chosen as the representative model organic pollutant, because there is a large amount of published work on this chemical, using more conventional reactor systems (Augugliero et al. [4], 2.0 dm³ batch STR; Okamoto et al. [5], 0.2 dm³ batch STR; Kawaguchi [11], 0.4 dm³ batch STR), with which studies in the CDCR may be compared. An initial phenol concentration of 100 mg/dm³ was used for all experiments. A Degussa P25 TiO₂ catalyst was used for all photocatalytic work.

The P25 catalyst had the following characteristics;

Catalyst	Particle Size (nm)	Catalyst Structure	Specific Surface area (m ² /g)	Particle Density (g/cm ³)
P25 TiO ₂	21	100% Anatase	50 ± 15	2.6

Catalyst loading was varied in the range of 0.01–0.1 w/w%.

For some experiments the pH of the reaction mixture was adjusted at the start of the reaction and monitored throughout the reaction. Solutions of 0.1 M H₂SO₄ and 0.1 M NaOH were used to change the pH. Reaction mixtures were studied with solutions of pH in the range 2.0 ≤ pH ≤ 12.0. Phenol and intermediate products were analyzed by HPLC (Waters 490E) fitted with a Nova-Pak C18 column, using a methanol/water mobile phase.

RESULTS

Complete mineralization of 100 mg/l phenol solutions was achieved in the CDCR when using a 1.0 kW UV lamp in very short irradiation times and under very mild reaction conditions (i.e., 1 barg and 40–50°C). Destruction of phenol was also achieved in the 30 W CDCR, but not complete degradation, as in the case of the 1.0 kW reactor. In most cases 40% breakdown of phenol was observed using the 30 W lamp in 150 minutes of irradiation (Boyes et al. [9]). The results obtained using different systems to generate hydroxyl radicals as oxidizing species are given in Table 2 and shown graphically in Figure 4.

The rate of reaction may often be limited by mass transfer of oxygen in the liquid phase. As an indication of the mass transfer capabilities and the intensive mixing generated by the CDC reactor, 24% of phenol was destroyed in 36 minutes using oxygen dispersion alone. In most cases, the intermediates formed included catechol, hydroquinone, benzoquinone, benzenetriol and pyrogallol. Figure 3 shows in detail an example of the rate of phenol breakdown and rate of formation of intermediates.

When UV was used alone, intermediates formed were more prominent and complete destruction of these intermediates was not achieved even though all the phenol was removed. When a combination of O₂ and UV was used, complete breakdown of phenol was achieved in less than 45 minutes of irradiation. Relatively rapid degradation of phenol itself was achieved with O₂/UV alone. Nevertheless, in these cases the intermediates were more refractory and the use of O₂/UV/TiO₂, whilst only increasing the

PRODUCT COMPOSITION Vs IRRADIATION TIME

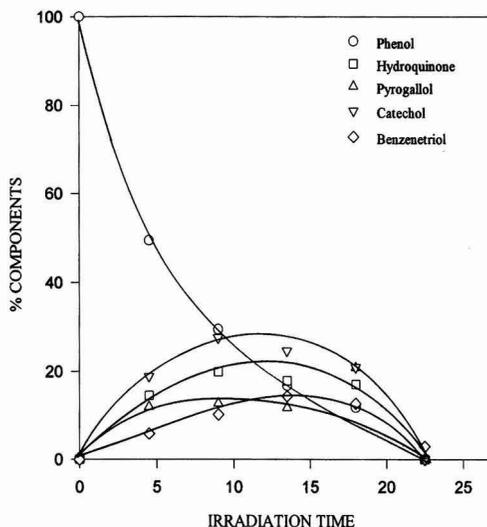


FIGURE 3 UV/TiO₂/O₂, W = 0.05 w/w%, pH 7.

TABLE 2. Breakdown of Phenol Solutions Using Different Processes in the 1 kW CDCR at pH=7.0 ± 0.5*

Process	pH	Phenol as a % of initial charge						T. B. (hrs)
		Time = 0 mins	Time = 9 mins	Time = 18 mins	Time = 27 mins	Time = 36 mins	Time = 72 mins	
O ₂	7.0	100	—	—	—	76.7	68.8	Not achieved
UV only	7.0	100	—	—	—	12.6	3.2	Not achieved
O ₂ /UV	7.0	100	—	—	—	1.2	0	3.5
O ₂ /TiO ₂	7.0	100	—	94.3	—	90.4	83.5	Not achieved
O ₂ /UV/TiO ₂ (W = 0.01 w/w%)	7.0	100	40.4	23.8	16.2	9.7	0	3.5
O ₂ /UV/TiO (W = 0.05 w/w%)	7.0	100	—	7.5	0	0	0	1.5
O ₂ /UT/TiO ₂ (W = 0.1 w/w%)	7.0	100	—	11.0	0.9	0	0	2

*T = 40 °C, W = 0.05 w/w%, Reactor charge = 10.0 dm³.

Time is given as irradiation time for Tables 2, 3, 4, 5 & 6, W = catalyst loading, Total Breakdown (TB) time is run time and not irradiation time for all Tables.

Breakdown of phenol using different processes

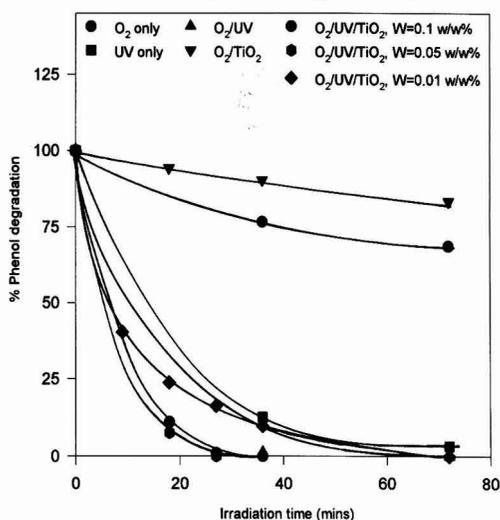


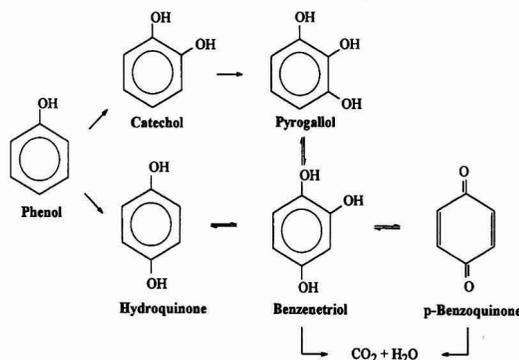
FIGURE 4 Phenol breakdown—pH 7.0, T = 40°C.

phenol degradation rate slightly, enhanced the rapid breakdown of the intermediate products.

Three catalyst loadings were used in this study (0.1, 0.05 and 0.01 w/w%) and from studies using the 30 W reactor, it is known that an optimum loading is required for a given UV source (i.e., 0.03 w/w% for 30 W reactor). High TiO₂ concentrations may decrease the interaction between photons and catalyst due to an increased extinction coefficient, subsequently reducing the reaction efficiency. Alternatively, a photocatalyst loading which is too low may lead to an insufficient concentration of activated catalyst sites for photocatalytic oxidation to proceed at any rapid rate. Studies suggest that 0.05w/w% is the optimum photocatalyst loading for the 1.0 kW reactor. When the lower catalyst

loading was used (0.01 w/w%) a slower rate of phenol breakdown was observed as compared with the rate of phenol breakdown when O₂ and UV was only used. This may be due to the O₂/UV system appearing to be very selective towards phenol destruction rather than intermediate product breakdown whereas the O₂/UV/TiO₂ system appears to be less selective, attacking phenol and intermediates at a similar rate.

From evaluated HPLC analysis and experiments involving the oxidation of individual intermediate products of phenol oxidation, the reaction scheme given below is suggested for phenol breakdown at pH 7.0. It is certain that other intermediates will be formed following ring opening but these were not detected during HPLC analysis. This may be due to their high reactivity leading to rapid removal with concentrations too low to detect. Studies of the oxidation of intermediates as starting compounds also indicated very rapid breakdown of intermediate products and further intermediate products were not detected. This type of observation was reported by Peral & Ollis [13] for a gas phase photocatalyzed m-xylene oxidation. The following reaction scheme is proposed for phenol oxidation in the CDCR.



Reaction Scheme for Phenol Degradation at pH 7.0

TABLE 3. Influence of pH on Phenol Breakdown in the 1.0 kW CDCR*

Process	pH	Phenol as a % of Initial Charge					T. B. (hrs)
		Time = 0 mins	Time = 9 mins	Time = 18 mins	Time = 27 mins	Time = 36 mins	
O ₂ /UV	4.0	100	35.3	3.8	0	0	2
O ₂ /UV	7.0	100	—	9.0	—	0	2
O ₂ /UV	10.0	100	60.8	18.8	2.4	0	2.5
O ₂ /UV	12.0	100	39.1	18.6	9.7	5.2	4
O ₂ /UV/TiO ₂	2.0	100	32.8	4.1	0	0	1.75
O ₂ /UV/TiO ₂	4.0	100	8.9	0.7	0	0	1.5
O ₂ /UV/TiO ₂	7.0	100	44.7	7.5	0	0	1.5
O ₂ /UV/TiO ₂	10.0	100	56.9	15.7	6.2	2.2	2.5
O ₂ /UV/TiO ₂	12.0	100	29.2	13.8	5.8	0	3.5

*T = 40°C, W = 0.05 w/w%, reactor charge: 10 dm³.

The oxidation processes are very sensitive to the pH of the aqueous system (Sharratt [7]) and the effects of low and high pH were studied for two different reaction systems employing O₂/UV with and without TiO₂ catalyst. The pH was adjusted using 0.1 M solutions of sulphuric acid and sodium hydroxide solutions. The results of pH studies in the 1.0 kW UV reactor are given in Table 3.

From Table 3, it can be seen that a more rapid rate of phenol degradation occurred for lower pH solutions, in particular at pH 4.0, where both O₂/UV and O₂/UV/TiO₂ systems gave best results. This effect is in agreement with other workers (Okamoto et al. [5]) and could be explained by the fact that pH values > 7.0 favor the formation of carbonate ions, which are effective scavengers of hydroxyl ions and can substantially reduce the efficiency of the oxidation process. The hydroxyl radical is unselective and will react readily with carbonate ions as well as with target components, reducing hydroxyl radical concentrations and rates of organic degradation. Carbonates are generated through the breakdown of organics, even in wastes which are initially free of carbonates. At pH 4.0, 91% phenol degradation in 9 minutes of irradiation was achieved in the CDCR when O₂/UV with TiO₂ catalyst was used and under these conditions is more effective than O₂/UV alone.

The addition of H₂O₂ has been observed to enhance oxidation rates for phenol oxidation in the presence of UV irradiation and is indicative of the role played by HO· radicals. The addition of 0.02 dm³ 28 w/v% H₂O₂ each hour was found to accelerate the rate dramatically and enabled total phenol degradation in the 30 W reactor. The total irradiation time required was also reduced by 50% (Boyes et al. [9]).

For studies in the CDC reactor fitted with the 1.0 kW UV lamp, 0.1 w/w% H₂O₂ was added to the start of each reaction in order to see what effect, if any the presence of H₂O₂ had on reaction rates. Initial oxidation rates for phenol oxidation were accelerated as compared with reactions without any H₂O₂ added to the reaction mixture. This supports strongly the proposal that the HO· radical is a key reactant in photooxidation since it will be generated by H₂O₂ scission. The results for the different reaction systems used with H₂O₂ are presented in Table 4. Hydrogen peroxide itself is a powerful oxidant with an oxidation potential of 1.77 eV, which in itself is able to destroy 14.5% phenol in 18 minutes of irradiation using only 0.1 w/w%. When H₂O₂ was added to both O₂/UV and O₂/UV/TiO₂ systems enhanced oxidation rates were observed.

This study concentrates mainly on the use of initial phe-

TABLE 4. Breakdown of Phenol Solutions Using Different H₂O₂ Processes in the 1 kW CDCR at pH=7.0 ± 0.5*

Process	Phenol as a % of Initial Charge						T.B. (hrs)
	Time = 0 mins	Time = 9 mins	Time = 18 mins	Time = 36 mins	Time = 54 mins	Time = 72 mins	
O ₂ only	100	—	—	76.7	—	68.8	Not achieved
UV only	100	—	—	12.6	—	3.2	Not achieved
H ₂ O ₂ only	100	—	85.5	79.8	76.0	74.6	Not achieved
UV/H ₂ O ₂	100	—	21.1	6.5	0	0	Not achieved
UV/H ₂ O ₂ /TiO ₂ (W = 0.05 w/w%)	100	—	22.7	8.0	0	0	Not achieved
O ₂ /UV/H ₂ O ₂ /TiO ₂ (W = 0.05 w/w%)	100	30.6	3.6	0	0	0	1.5
O ₂ /UV/TiO ₂ (W = 0.05 w/w%)	100	44.7	7.5	0	0	0	1.5

*T = 40°C, reactor charge = 10.0 dm³. H₂O₂ concentration = 0.1 w/w% of feed added at start only.

TABLE 5. Breakdown of Phenol Solutions Using Different Initial Phenol Concentrations at pH=7.0 ± 0.5*

Process	Phenol Concn.	pH	Phenol as a % of Initial Charge						
			T = 0 mins	T = 9 mins	T = 18 mins	T = 27 min	T = 36 mins	T = 72 mins	T = 144 mins
O ₂ /UV/TiO ₂	50 mg/l	7.0	100	6.3	0	TB	—	—	—
O ₂ /UV/TiO ₂	100 mg/l	7.0	100	44.7	7.5	0	TB	—	—
O ₂ /UV/TiO ₂	1000 mg/l	7.0	100	—	72.4	—	62.1	40.0	26.4
O ₂ /UV/TiO ₂	1000 mg/l	4.0	100	—	66.5	—	50.1	28.9	12.5

*Reactor charge = 10.0 dm³. (T = 40°C, W = 0.05 w/w%).

TABLE 6. Breakdown of Phenol Solutions Using Air in the 1 kW CDCR at pH=4.0 ± 0.5*

Process	W w/w%	pH	Phenol as a % of Initial Charge				T.B. (hrs)
			T = 0 mins	T = 9 mins	T = 18 mins	T = 36 mins	
Air/UV/TiO ₂	0.05	4.0	100	26.6	23.8	0	3
O ₂ /UV/TiO ₂	0.05	4.0	100	8.9	0.7	0	1.5

*Reactor charge = 10.0 dm³.

TABLE 7. Mols of Phenol Reacted per mol of Photon (for Initial Rate Conditions)

Process	pH	Mol Phenol/Mol of Photon
UV	7.0	0.20
O ₂ /UV	4.0	0.39
O ₂ /UV	7.0	0.45
O ₂ /UV/TiO ₂	4.0	0.74
W = 0.05 w/w%		
O ₂ /UV/TiO ₂	7.0	0.45
W = 0.05 w/w%		

nol concentrations of 100 mg/l, but some studies were conducted using 50 and 1000 mg/l and these results are shown in Table 5. Using low phenol loadings (< 100 mg/l), total breakdown of all organic materials was achieved in very short times. Using very high phenol loadings led to 88% of phenol being destroyed in 144 minutes of irradiation time. Total breakdown would have been achieved with longer irradiation times.

Due to the greater expense of using pure oxygen for oxidation processes, an experiment using air as the oxidant was undertaken, using the most favorable conditions previously observed when using pure oxygen (i.e., pH 4.0, W = 0.05 w/w%). Using air in the CDC reactor, total degradation of all organic material was achieved in approximately twice the time required when using pure oxygen. The use of pure oxygen is not a disadvantage in the CDC as compared with other processes. This is due to the capability of the CDC to ensure 100% gas utilization, thus ensuring that no oxygen is wasted. However, if oxygen is used, there must be a source, whereas air is available at any location.

The quantity of light photons by irradiation and impinging within the reaction zone, the Photon Flux, was determined using an actinometer (Murov [10]). The following

values of photon flux were determined for the different lamps used with the CDC reactor;

Reactor lamp	Photon flux Einsteins/s
30 W	1.06 × 10 ⁻⁶
1.0 kW	2.91 × 10 ⁻⁵

With the calculated values of photon flux measurements, the mols of phenol reacted per mol of photon were evaluated for the reaction systems studied (see Table 7). The O₂/UV/TiO₂ reaction system at pH 4.0 gave the greatest photon efficiency for a catalyst loading of 0.05 w/w%. This is in agreement with previous results which show that the greatest degradation of phenol and all intermediates in the shortest irradiation time is given by the O₂/UV/TiO₂ system.

The CDC reactor equipped with both 30 W and 1.0 kW lamps has proved to be highly effective in the total degradation of phenolic waste. The very high mass transfer efficiency and mixing achieved in the CDC reactor aids chemical reaction and enables reaction to occur in very short irradiation times. However, it is not possible to compare easily the work with that of Baba et al. [12] who used a low pressure UV source with a different UV frequency (350–400 nm). Nevertheless, it is likely that the mass transfer efficiency for the CDCR is far superior.

FUTURE WORK

Future work will include the development of a rate equation for various variables on the oxidation rate of phenol from detailed kinetics currently being investigated. The studies presented here will be extended to the use of ozone (O₃) with and without the presence of a suitable catalyst and a range of organic pollutants will be studied including chlorophenols and dioxanes. Dioxanes will be investigated

to enable a direct comparison of the reaction rate at similar reaction conditions to the work of Sharratt [7]. This will provide an indication of the mass transfer effectiveness of the CDCR.

LITERATURE CITED

1. **Boyes, A. P., et al.**, "The Cocurrent Downflow Contact Reactor (CDC) as a Fixed Bed and Slurry Reactor for Catalytic Hydrogenation," *J. Chem. Tech. Biotech.*, **64**, pp. 55-65 (1995).
2. **Herrmann, J. M., et al.**, "Heterogeneous Photocatalysis: An Emerging Technology for Water Treatment," *Catalysis Today*, **17**(1-2), pp. 7-20 (1993).
3. **Serpone, N., et al.**, "Heterogeneous Photocatalysed Oxidation of Phenol, Cresols and Fluorophenols in TiO₂ Aqueous Suspensions," in *Photosensitive Metal-Organic Systems: Mechanistic Principles and Applications*, C. Kotal and N. Serpone, eds., ACS Advances in Chemistry Series, Vol. 238, pp. 281-314 (1993).
4. **Augugliero, V., et al.**, "Photocatalytic Degradation of Phenol in Aqueous Titanium Oxide Dispersions," *AIChE Journal*, **37**(7), pp. 89-109 (1988).
5. **Okhamoto, K., et al.**, "Heterogeneous Photocatalytic Decomposition of Phenol over Anatase TiO₂ Powder," *Bulletin Chem. Soc. Japan*, **58**, pp. 2023-2028 (1985).
6. **Bard, A. J.**, "Photoelectrochemistry," *Science*, **207**, 139-144 (1990).
7. **Sharratt, P.**, "Advanced Oxidation Processes for the Treatment of Aqueous Wastes," *Effluent Toxicity and Treatability*, UMIST Conference Centre, pp. 4.1-4.9 (Nov. 8, 1995).
8. **Cotton, F. A., and G. Wilkinson.** *Advanced Inorganic Chemistry*, 3rd edition, Wiley (1980).
9. **Boyes, A. P., et al.**, *Water Pollution III, Modelling, Measuring & Prediction*, L. C. Wrobel and P. Latinopoulos, eds., pp. 313-320 (1985).
10. **Murov, S. L.**, *Handbook of Photochemistry*, Marcel Dekker Inc. (1973).
11. **Kawaguchi, H.**, "Photocatalytic Decomposition of Phenol in the Presence of Titanium Dioxide," *Environ. Technol. Lett.*, **5**, pp. 471-474 (1984).
12. **Baba, S., et al.**, "Photocatalytic Degradation of Organics in Water," IChemE Research Event, Cambridge, UK, pp. 25-29 (1991).
13. **Peral, J., and D. F. Ollis.**, "Heterogeneous Photocatalysed Oxidation of Gas Phase Organics for Air Purification: Acetone, 1-Butanol, Butyraldehyde, Formaldehyde and m-Xylene Oxidation," *J. Catal.*, **136**, p. 554 (1992).

New Techniques for Solvent Recovery and Elimination of Wastewater Emissions During Vacuum Process Operations

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The pharmaceutical and chemical process industries are concerned with controlling volatile organic compound (VOC) emissions for several reasons: to meet environmental regulations, for increased worker safety, and to minimize product losses. Various methods can be used including flaring and carbon adsorption. These techniques are end-of-the-pipe solutions and are not integral with the process operation itself.

An improved technique for the recovery of solvents during reaction, distillation, evaporation, drying, filtration, mixing, and other vacuum operations is the APOVAC vacuum/gas compressor system. The skid-mounted, engineered package is based upon a single stage liquid ring vacuum pump. The system allows for the recovery and reuse of clean solvent with minimum air emissions and zero liquid emissions. VOC and biological oxygen demand (BOD) regulations are met by this technology.

The paper reviews the technical details of the system and presents test results and on-site operational data. Specific case histories involving methylene chloride recovery and acid/toxic gas neutralizations are also included.

In the chemical processing industry (CPI) the generation of vacuum is a necessity. Many chemical processes take place more easily, more quickly and more efficiently under vacuum than under atmospheric pressure, thus allowing better product quality at lower production cost. If it is a "wet" process involving the use of solvents then solvent recovery becomes an important consideration because of cost savings associated with its recovery as well as environmental benefits.

These objectives have stimulated the development of the APOVAC system concept which is based on the principle of closed loops or circuits. Since its development, the APOVAC system has enhanced today's chemical process technology through solvent recovery and recycling, elimination of wastewater effluent, and reduction of gas emissions thus contributing to a technically efficient and environmentally acceptable operation.

APOVAC SYSTEM CONCEPT

The underlying design of the APOVAC system is the combination of vacuum generation and solvent recovery through condensation in a closed circuit system composed

of a liquid ring vacuum pump (LRVP) plus a subsequent cooler. The incoming gas stream is cooled in the LRVP and loses its solvent load during the passage through the pump and the subsequent ring-liquid cooler. Condensation occurs in the system due to compression and cooling in the pump. The ring liquid and condensate (solvent) are collected in a central collection tank which is combined with the system ring liquid cooler where the temperature rise due to the pumping and condensation process is eliminated. An optional exhaust gas cooler further reduces the exhaust gas temperature and provides additional condensation. For the liquid components, the ring liquid is the same as the process solvent such that the latter can then be recycled directly into the production process since it is free from any contamination.

In this basic APOVAC system, three closed circuits exist.

- an internal ring liquid circuit between the pump and the cooler
- an external process liquid (solvent) circuit between the APOVAC system and the chemical processing unit
- an external cooling medium circuit between the APOVAC cooler and the coolant supply

The APOVAC system is self-contained, free from internal contamination, and requires, for its proper functioning, only energy for pumping and cooling. As an addition to a wet process chemical production unit, it allows the efficient recovery and recycling of solvents thus helping to reduce production cost, consumption of energy and solvent, and environmental pollution.

APOVAC SYSTEM DESIGN

Liquid Ring Vacuum Pump Features

The central part of any APOVAC system (Figure 1) is the liquid ring vacuum pump (LRVP) (Figure 2). A vaned impeller rotates eccentrically in a cylindrical housing with cyclically increasing and decreasing gas chambers to generate a suction and a compression area in the pump. A rotating liquid ring acts as a sealant between the impeller and the housing. In this context, the LRVP is the component of choice because of its vacuum generation capability and its various other functions as outlined below:

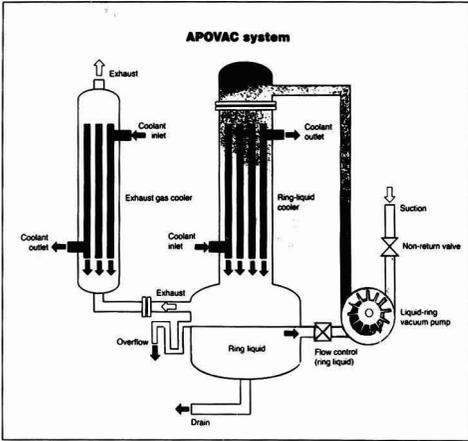


FIGURE 1 Schematic representation of the APOVAC system.

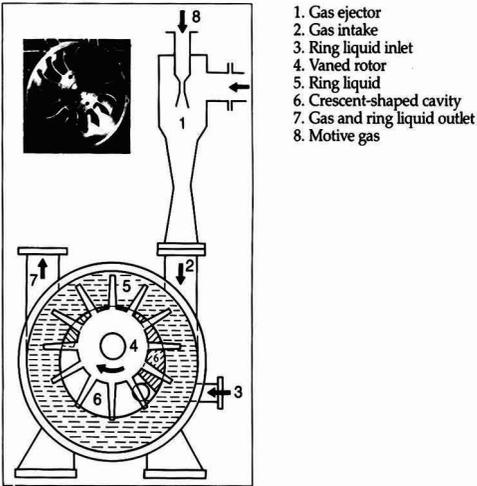


FIGURE 2 Operating principle of liquid ring vacuum pump with upstream gas ejector.

- heat exchanger function due to the thorough mixing effect between ring liquid and conveyed gas resulting in a strong cooling effect and a nearly isothermal gas compression
- condenser function due to compression and cooling of the gas stream
- reactor function between ring liquid and conveyed gas for neutralization
- tolerance to liquids and solids which may enter the pump
- capability to work as a vacuum pump or as a compressor

Functional System Concept

These useful features of liquid ring vacuum pumps allow APOVAC systems to be designed to a small number of simple but very efficient principles:

- Combination of functions:
 - Pump: condenser; cooler; reactor; gas conveying unit for pressure and vacuum service
 - Ring liquid: solvent; condensate
 - Cooler/Tank: cooling unit for ring liquid; condenser for solvent; collector for ring liquid and solvent condensate
- Separation of functional elements: Separate circuits for cooling media avoid contamination of process liquids and allow different temperature levels in different system stages.
- Integration in closed circuits: Several closed circuits maximize reusability of process liquids and minimize internal contamination and losses.
- Flexibility and adaptability: The APOVAC system and its components can easily be adapted or modified relative to size, ring liquid requirements, materials choice, control devices, accessories, etc. according to user requirements.

Gas Temperature Profile and Energy Balance

Since condensation is generally the critical process step of any APOVAC system, its temperature profile at a given operating pressure level is of vital interest (Figure 3). In each APOVAC system, three different temperature levels prevail. An optional exhaust gas condenser would increase this number to four. The incoming gas stream of a temperature T_1 is cooled in the pump through its contact with the ring liquid and leaves the pump discharge together with part of the ring liquid at the temperature T_2 . In the subsequent countercurrent ring liquid cooler, the gas temperature drops down to T_3 . If an exhaust gas condenser exists, another cooling step down to T_4 takes place. The liquid ring temperature in the system oscillates between T_2 and T_4 as a consequence of the energy-dissipating pumping process on the one side, balanced by the cooling performance of the liquid ring cooler on the other side.

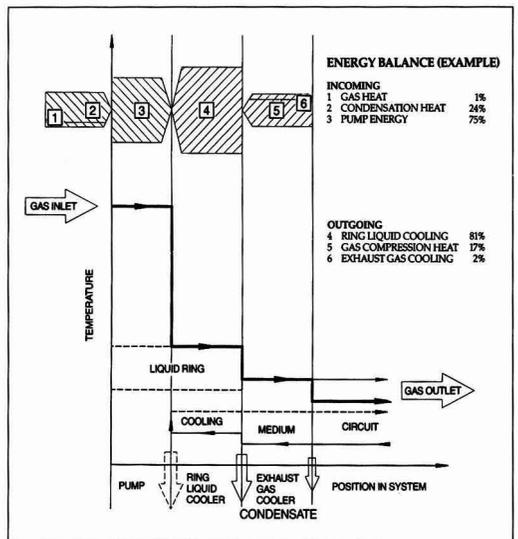


FIGURE 3 Gas temperature profile and energy balance for APOVAC system.

TABLE 1. Energy Balance

INCOMING	% OF TOTAL	OUTGOING	% OF TOTAL
Gas Heat	1%	Gas Compression Energy [†]	17%
Solvent Cond. Heat	24%	Ring Liquid Cooling Energy	81%
Pumping Energy	75%	Exhaust Gas Cooling	2%

TABLE 2. CAA Title III's "Most Wanted" List

Acetaldehyde	Dimethyl phthalate	Phthalic anhydride
Acrylic acid	Epichlorohydrin*	Propylene oxide
Acrylonitrile*	Ethyl benzene*	Styrene*
Allyl chloride	Ethyl chloride*	Styrene oxide*
Aniline*	Ethylene dichloride*	perchloroethylene*
Benzene*	Ethlene glycol*	Titanium trichloride
Benzyl chloride	Ethylene oxide	Toluene*
1, 3-Butadiene	Formaldehyde	Trichloroethylene*
Caprolactam	Glycol ethers*	Vinyl acetate
Carbon tetrachloride*	Hydrochloric acid	Vinyl bromide
Chlorine	Maleic anhydride	Vinyl chloride*
Chlorobenzene*	Methanol*	Xylenes*
Chloroform*	Methyl methacrylate	Hydrofluoric acid
Cresols/cresylic acid	Methylene chloride*	
Cumene	Phenol*	
Diethanolamine*	Phosphorus	

*Solvents typically used as ring liquids in the APOVAC unit.

The energy balance of a typical APOVAC system handling inert gases saturated with solvents must consider several elements, as shown in Table 1. The relative size of each element for air at 10°C saturated with water is also given. It is important to note that the solvent recovery rate of the APOVAC system at a given pressure level depends primarily on the temperature of the exhaust gas.

The APOVAC design ensures the discharge of the gas stream at the lowest possible system temperature (i.e., after the ring liquid cooler).

ENVIRONMENTAL CONTROL: AIR AND WASTEWATER

A plant site is required to meet many environmental rules for air emissions and wastewater emissions. The new Clean Air Act (CAA), for example, will be tougher than ever and will require a 90% reduction in emissions by the year 2000 for 189 major chemicals, Table 2. Of these compounds, over 50 percent are solvents that are typically used as ring liquids in the APOVAC system. In terms of wastewater emissions, the Clean Water Act allows a plant to discharge only the pollutants that are contained in its permit.

There are many ways to address VOCs and other forms of air pollution. Solutions include carbon adsorption systems, scrubbers, catalytic oxidation, and thermal incineration with regenerative heat recovery. For wastewater control, filtration, distillation, settling tanks, and chemical treatment are common techniques.

The above discussion focuses on pollution control as an end-of-the-pipe solution and looks at each waste stream as an individual problem. The most effective approach for environmental control is a "total-system" view point. The APOVAC system solves both the air and wastewater prob-

lem as part of the process solution. Wastewater emissions are eliminated as the ring liquid is the same solvent as the process fluid.

VOC rules are met by the uniquely designed ring liquid cooler operating on the high pressure side of the LRVP. Table 3 illustrates the dramatic effect of this cooler on the exhaust gas solvent load for different solvents. Finally, for difficult or high-load solvent recovery, a precondenser or exhaust gas condenser can be added. The following sections illustrate examples of a total process approach to solving a pollution problem, rather than a quick (and expensive) fix to a specific exhaust stream emission problem.

AREAS OF APPLICATION

Drying: The APOVAC system operates as a vacuum pump with solvent recovery for conventional vacuum drying. In addition, it can be used as a compressor for filter-cake "blowing" and/or convection drying. In these applications, emissions can be virtually eliminated by circulating an inert gas, usually N₂, with intermediate condensation at elevated pressure and low temperature. In convec-

TABLE 3. Exhaust Gas Load as Percentage of 1 Kg Air

Ring liquid	(°C)	Circulation without gas cooling	APOVAC Unit
Acetone	-15	19.8	6.3
Methyl alcohol	-5	8.6	2.5
Toluene	+10	12.2	3.3
Butyl alcohol	+20	8.5	2.7

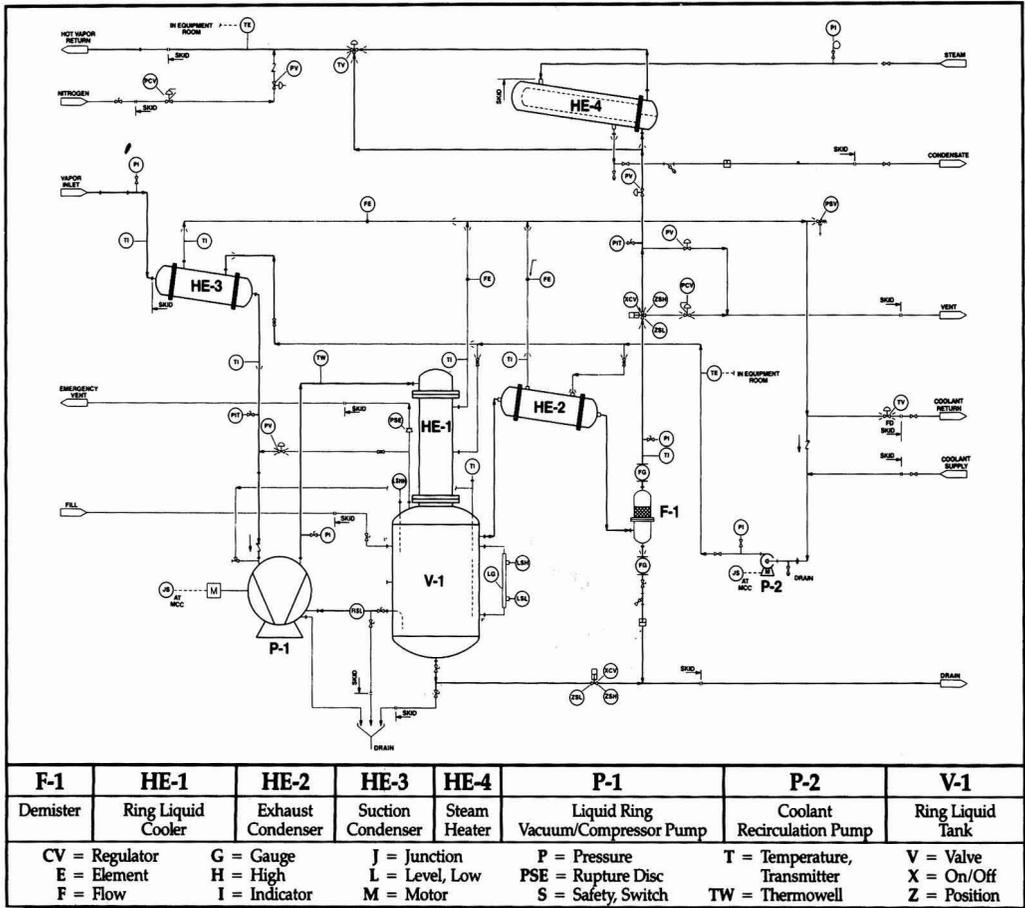


FIGURE 4 APOVAC solvent recovery skid for vacuum and convection (pressure) drying.

tion drying, the gas is reheated before re-cycling to the dryer or filter-dryer. This is shown in Figure 4.

Distillation: Running these processes under vacuum lowers the distillation temperature and helps save costs. APOVAC units generate the required vacuum and recover evaporated condensables carried away with the air leakage.

Crystallization: Crystallization in wet processes requires the removal of solvents. The crystallization process is often accelerated or better controlled under vacuum. The APOVAC units ensure the necessary vacuum plus the recovery of the process liquids.

Stripping of Solvents (Recovery of Solvents from Waste Air Streams): In the case of adsorption, solvents are attached to a suitable medium, e.g. activated carbon. When the adsorptive capacity is reached, the solvent must be removed and ideally recovered. This is often achieved by applying heat and vacuum or pressure. APOVAC units generate vacuum and/or pressure and recover the solvents released. APOVAC compressor systems in addition allow a smaller sized system, and more efficient solvent recovery than non-pressurized systems. Finally, as pretreatment for waste air streams prior to the end-of-pipe installation, they recover between 60 to 90 percent of the solvent load, thus reducing the burden on final gas treatment unit.

Degassing of Extruder, Kneader, and Compounding Units: Many chemical compounds contain a certain amount of volatile compounds from their manufacturing process. During thermal and mechanical processing like extrusion, kneading, and compounding these volatiles are released, especially at elevated temperatures, and must be removed. The removal process is helped significantly by the

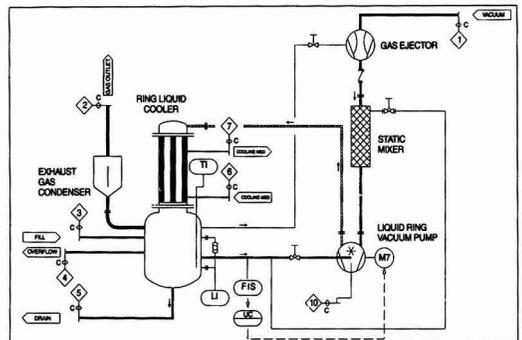


FIGURE 5 APOVAC scrubbing skid for acid gas neutralization.

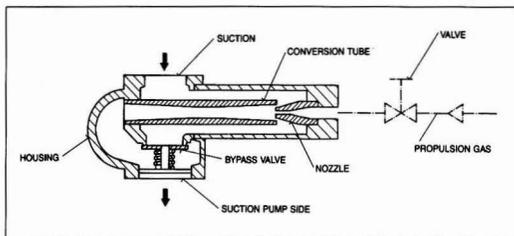


FIGURE 6 Gas ejector using system gas-vapor as the motive (propulsion) force.

application of vacuum. APOVAC systems generate the vacuum and recover the condensable part of the volatiles. The tolerance of a liquid ring pump to small particles which are frequently released is an additional benefit.

Waste Air & Water Scrubbing for Neutralization and Purification: The close contact of the conveyed medium with the ring liquid allows specific reactions to take place in the pump such as neutralization of acids or deodorization of odorous gas streams. In the former, the ring liquid is a caustic solution which, in contact with the acid gas stream, results in the removal of the acid and the formation of salts in the ring liquid. The ring liquid has to be treated regularly to remove the salt generated. A similar purification effect can be achieved with odorous gas streams through a ring liquid to scrub the process gas upstream of the pump significantly helps to increase the neutralization efficiency. This is shown in Figure 5.

Chemical Vapor Deposition: In this metal coating process, compounds of metals like aluminum, titanium and others, are deposited on the desired materials. The resulting process acid gases can be neutralized in APOVAC systems using an alkaline ring liquid.

High Vacuum Applications: For applications that demand increased vacuum, a fully integrated gas ejector can be incorporated as shown in Figure 6. This ejector design uses the vapor in the gas/vapor space of the collector tank as the motive gas force. The result is increased vacuum without the use of fresh air or nitrogen. Organic emissions and gas consumption are reduced as compared to conventional air or steam jet ejector systems. Finally, a blower can be added for higher vacuum levels.

Replacement of Existing Vacuum Systems: The APOVAC unit can replace existing steam jets where there is high water usage, environmental problems, or inefficiencies. For conventional oil vacuum pumps, replacement with an APOVAC unit can eliminate oil contamination problems as well as the high maintenance costs associated with these systems.

CASE HISTORY INSTALLATION: METHYLENE CHLORIDE RECOVERY

In this batch-granulation process, 200 Kg of MeCl_2 is emitted. Solvent recovery is required due to environmental rules as well as for process economics. The user installed an APOVAC 2510 system with a precondenser, demister, exhaust condenser, and back pressure control. The ring liquid is MeCl_2 with a chilled brine at -40°C as the coolant. The result is pure MeCl_2 recovery of greater than 96 percent, which is reused in the process.

A second installation of interest is a methylene chloride recovery/neutralization application. In this case, the appli-

cation is a monomer batch reaction where 196 Kg of MeCl_2 is steam-stripped at a final vacuum of 5 mm Hg. The issue facing the plant was that approximately 70 percent of the MeCl_2 was lost to the atmosphere and the wastewater disposal system through the steam jets. A further complication was the presence of 5 percent water in the solvent, thus eliminating low temperature condensing as an option.

After conducting on-site test work, the user installed an APOVAC 2510 with an exhaust condenser and gas ejector. The ring liquid is a 40 percent solution of potassium carbonate (K_2CO_3), and the coolant is at 0°C . The K_2CO_3 ring liquid provides for a phase separation as MeCl_2 is not soluble in K_2CO_3 . The MeCl_2 is decanted from above the K_2CO_3 in the receiver tank. Finally, the K_2CO_3 neutralizes the trace hydrochloric acid that is formed by the aqueous MeCl_2 . The user recovered greater than 90 percent of the MeCl_2 and eliminated wastewater emissions of an $\text{MeCl}_2/\text{H}_2\text{O}$ mixture by replacing the steam jets.

SUMMARY

This paper examined an approach to solving an emission problem that goes beyond a single-stream response. The CAA allows for site-specific issues to impact the selection of a control device. These include utility requirements, space, work force skill, disposal options, and secondary environmental impacts, such as wastewater and solids generation by the proposed equipment. The APOVAC unit addresses these issues and allows the user to solve an air and wastewater emission problem simultaneously with a single control device. This overall emission minimization approach provides benefits to several different groups associated with the plant and allows for a pro-active response to pollution control.

LITERATURE CITED

1. **Bays, J. N.**, "Minimizing Wastes from Vacuum Pumping Systems," *Chemical Engineering*, pp. 124-130 (October, 1996).
2. **Faragallah, W. H.**, *Liquid Ring Vacuum Pumps and Compressors*, Translated from German by David Hollywood and Anette Vogt (1995).
3. **Kalman, A., J. D. Westbrook**, "Recent Development in Recycle Drying for Batch Processing Industry," presented atACHEMA, (June, 1988).
4. **Kocwin, M. T.**, "Liquid-Ring Pumps for Handling Gases and Vapours," *Sulzer Technical Review*, p. 63, No. 2 (1973).
5. **Perlmutter, Barry A.**, "Combined Filter-Dryer Process Unit Improves Product Quality and Reduces Production Time," *Pharmaceutical Engineering*, p. 42-45 (July/August, 1989).
6. **Rader, Mutsakis, Grosz-Ruell**, "Better Adsorption: Try a Static Mixer," *Chemical Engineering*, p. 137-142 (July, 1989).
7. **Ryans, J. L. and D. L. Roper**, "Process Vacuum Systems Design and Operations," McGraw-Hill, New York (1996).
8. **Sobieszek, T.**, "Environmentally-compatible Evacuation of Gases and Vapours," *Sulzer Technical Review*, p. 27 ff, No. 4, (1986).
9. **Zahodiakin, P.**, "Puzzling Out the New Clean Air Act," *Chemical Engineering*, pp. 24-27 (December, 1990).

Reductive Dehalogenation of Trichloroethylene Using Zero-Valent Iron

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Reductive dehalogenation of hazardous organics using zero-valent metals is a promising technology. The purpose of this study was to examine the effect of feed concentration, initial pH, metal loading and particle size of metal on the degradation of trichloroethylene (TCE), using zero-valent iron. The degradation rate was found to be first order with respect to the organic molecule, thus the conversion was independent of initial TCE concentration. The amount of TCE degraded at any given time was found to be directly proportional to the dissolved iron in solution. The metal surface area plays a crucial role in the process. Two fold increase in the pseudo first order rate constant was obtained when the metal particle size was decreased from 370 μm by factor of 2.5. For iron surface area per unit volume (S/V) of solution $< 1000 \text{ m}^{-1}$, the TCE degradation rate constant increased linearly with S/V ratio.

INTRODUCTION

Trichloroethylene (TCE), a chlorinated aliphatic organic compound has been widely used in the industry as a universal degreasing agent and for cleaning purposes due to its unique properties. This extensive use of TCE combined with historical waste-disposal practices and its persistence in the hydrogeological environment, has resulted in its widespread occurrence in groundwater. Epoxidation of TCE by liver oxidation enzymes produces carcinogenic compounds. Thus, TCE presents a serious environmental concern due to its toxicity and hence considerable research has been focused on the development of remedial technologies to remove TCE from groundwater. A commonly used method for remediating contaminated groundwater, the pump and treat technology, pumps water from the ground and treats it *ex-situ*. The *ex-situ* treatment may involve air stripping [8, 14], granular activated carbon adsorption (GAC) [14], etc. However, these technologies do not destroy TCE but simply transfer it to another medium. TCE can be destroyed by advanced methods like oxidation using ozone with ultraviolet light and hydrogen peroxide [7]. These alternatives are cost intensive and difficult to use *in-situ*. Biodegradation [20], of TCE under aerobic [15], and anaerobic [5], conditions has also been reported. These fortuitous metabolisms however, need xenobiotics

like toluene or phenol [9] for the induction of the required enzymes in certain methanogenic microorganisms and these biological processes are very slow.

All these pump and treat technologies involve high capital and energy costs. Moreover, these are less efficient as a substantial amount of uncontaminated groundwater is removed along with the contaminated water. As a result, the priority of treatment is now shifting to *in-situ* treatment. Reductive dehalogenation using non toxic zero-valent metals (such as Fe) is one such emerging technology.

REDUCTIVE DEHALOGENATION USING METALS

Zero-valent metals are effective in enhancing the rate of degradation of a wide range of halogenated compounds. Ions dissolve from the metal surface, releasing electrons which provide energy for the dehalogenation process. The use of zero-valent metals, mainly Fe, Sn and Zn, to remediate water containing chlorinated hydrocarbons has been proposed by several researchers. Research emphasis has been focused on the use of iron as the metallic catalyst [4], or a modified iron, such as the palladium plated iron granules used by Korte *et al.* [10]. Boronina *et al.* [2], have demonstrated the efficacy of using Zn or Sn as the catalytic metal, and showed that relatively fast reaction rates can be obtained using very fine Zn particles in an inert atmosphere.

The destruction of chlorinated species into metal salts and dechlorinated byproducts has been shown to occur at reaction rates ranging from 5 to 15 orders of magnitude faster than those observed for natural abiotic processes [16]. O'Hannesin *et al.* [16], have shown that a reactive bed containing Fe filings was able to remove 90% of the TCE from groundwater at the Canadian Forces Base, Borden, Ontario site. They concluded that the reaction rate was independent of TCE concentration. In further studies, chlorinated species were destroyed by granular iron for most halogenated methanes, ethanes, and ethenes [6]. Matheson and Tratnyek [13], studied the degradation of chlorinated methanes using iron metal and suggested the possibility of a direct electron transfer mechanism.

In building a pilot scale operation for the reduction of TCE using iron fillings, MacKenzie *et al.* [12], determined several controlling factors. Catalytic bed life was affected by the alkalinity of the ground water being treated, and the amount of dissolved oxygen in the water. The presence of carbonate or oxide forming species in the water leads to an inert layer of metal oxide or metal carbonate forming on

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the metal surface. This layer greatly reduces the overall reaction rate [1, 11, 12, 18]. MacKenzie et al. [12], found that a ten fold increase in aqueous alkalinity reduced the reaction rate by three fold.

Metallic surface area is a controlling factor in the rate of reaction [1, 18]. Boronina et al. [2], have shown that cryo-particle (cryo particles are the particles prepared by cryo method yielding very high surface area) Zn with a surface area $> 65 \text{ m}^2/\text{g}$ reduced the concentration of CCl_4 in water by over 90% in three hours, while granular Zn, having a surface area $< 1 \text{ m}^2/\text{g}$, achieved a reduction of only 25%. A similar correlation between surface area and dechlorinating ability was seen in studies using Sn.

The reduction mechanism is still not well understood. Moreover, this reaction is quite slow and depends on several parameters like pH, temperature, and most importantly, surface area of the metal under consideration. The purpose of the present study was to investigate the effect of parent TCE concentration, initial pH, metal dissolution, and surface area of metal on the degradation rate of TCE using zero-valent iron to get an insight into the mechanistic aspects of the reaction.

EXPERIMENTAL

Batch runs were carried out in the laboratory for the degradation of trichloroethylene (TCE) using zero-valent iron. Known amount of 100 mesh iron (150 μm) and 40 mesh iron (370 μm , for selected experiments) electrolytic iron powder (obtained from Fisher Scientific Inc., used without any pretreatment) was added to 40 ml glass hypovials. The hypovials were then filled with TCE solution of known concentration in deionized water, leaving no headspace and were sealed immediately with caps containing Teflon-lined septa. To carry out experiments under deoxygenated conditions, appropriate amount of sodium bisulfite was added to the hypovials before sealing. The hypovials were then placed in an incubator shaker (150 rpm) allowing for complete mixing. At varying times, a set of two hypovials was removed from the shaker and sub-samples were transferred to vials for extraction. The remaining solution was analyzed for pH, dissolved iron and chloride removal. n-Pentane was used to extract the organic compounds from aqueous solution with water/pentane ratio of 1:1. Samples were shaken by hand for 5 minutes to allow for equilibration between water and pentane phases. For analysis, a $1 \mu\text{l}$ aliquot of equilibrated pentane was removed and directly injected into a HP 5890 Gas Chromatograph with J & W Scientific DB-624 (ID-0.25mm, length-30m) column. The chromatograph was equipped with a MS detector. EPA 624 method was used for analysis of volatile organic compound with following conditions: Oven Temperature of 35°C (4 minutes) to 200°C at $6^\circ \text{C}/\text{min}$., carrier gas-zero grade Helium with flow rate 7.5 ml/min., MS scan range $m/z = 35 - 260$ at 0.6 sec/scan. At lower concentrations of TCE, water to pentane ratio was increased to improve analytical sensitivity. Detection limit for TCE with this procedure was 0.8 mg/L. The analytical error was typically in the range of $\pm 8\%$.

Chloride analysis in the aqueous phase was done using an Orion Combination Chloride electrode (model 96-17B). Samples were occasionally spiked with NaCl standards to ensure that no interference was caused by the formation of intermediates. The analytical error was less than 5%. pH

measurements were carried out using a digital pH meter. Dissolved iron in the solution was determined using an Inductively Coupled Plasma Spectrophotometer (ICP-2500).

RESULTS AND DISCUSSION

Degradation of TCE and Chloride formation

A typical concentration profile resulting from the batch tests is shown in Figure 1. As seen from the figure, the concentration of TCE in the control (no iron) hypovials remained nearly constant over the duration of the experiment. The concentration in the hypovials containing iron however showed an exponential decline. This decline is initially fast but slows down considerably as time progresses. This tailing may be due to the mass transfer limitation caused by the formation of possible precipitates on the iron surface. The free chloride formed during the process is plotted as the percentage of maximum chloride that can be formed from the parent TCE (Figure 1). It is interesting to note that though close to 20% of starting TCE was degraded in the first 10 hours, no appreciable chloride formation was observed during the same time. Dissolved oxygen accounts for this particular lag period observed in the chloride formation. Experiments carried out in the absence of dissolved oxygen (achieved by adding sodium bisulfite) show concerted chloride formation with TCE decline (Figure 1). Oxygen thus acts as a competitor to TCE in accepting electrons released to the solution by metal dissolution. Although close to 90% degradation was observed at the end of the experiment, the free chloride formation observed was just 57% of the maximum attainable. To test the hypothesis if this was due to the formation of precipitates on the surface of iron, the iron was replaced at the end of 120 hours, after which no more change in the chloride concentration was observed. However the maximum chloride formation was still the same (Figure 2). Moreover, maximum chloride formation was independent of initial concentrations of TCE as shown in Figure 2. The data fits the pseudo first order model and this rate constant is independent of the initial TCE concentrations (Figure 3), which is a typical characteristic of first order reactions. The rate constant found was 0.21 /h for 100 mesh iron particle size and this value

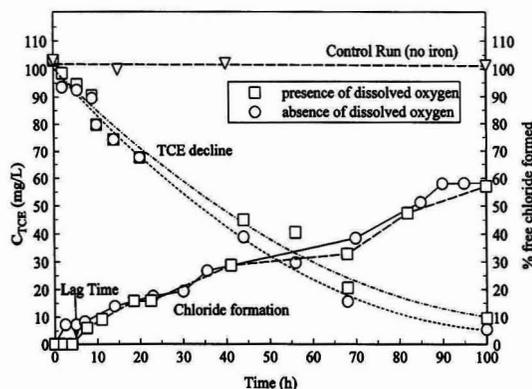


FIGURE 1 A typical concentration profile of trichloroethylene (TCE) and free chloride obtained in batch experiments. Initial conditions: TCE = 103 mg/L, pH = 6.25, Iron = 250 gm/L

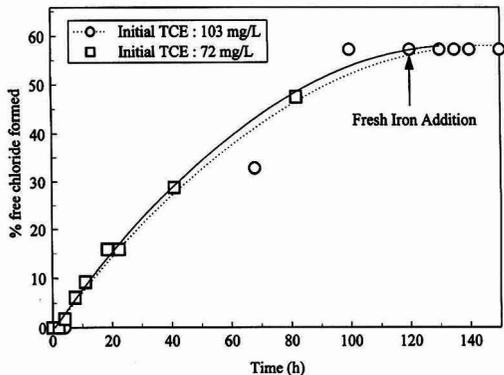


FIGURE 2 Effect of initial Trichloroethylene (TCE) concentration on chloride formation. Initial conditions: pH = 6.25, Iron = 250 gm/L

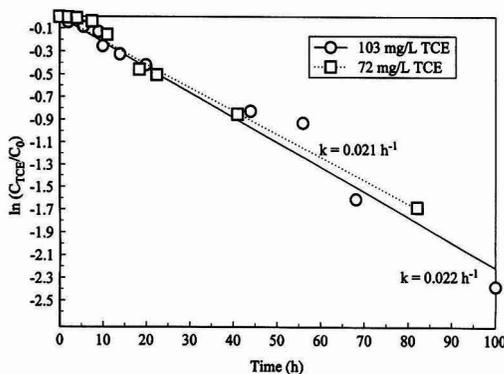


FIGURE 3 Effect of initial trichloroethylene concentration on reaction rate constant. Initial conditions: pH = 6.25, Iron = 250 gm/L

matches well with published data [6]. The observed rate constant (not shown) was the same for experiments carried out under deoxygenated conditions. The rate of dechlorination of TCE is thus not affected by the presence of dissolved oxygen in the solution.

Effect of initial pH

The pH of the solution decreased gradually with reaction time and then showed a slight increase (Figure 4). Experiments conducted at two different initial pH values—4.64 and 6.25, however did not show a significant effect on the rate of the degradation process. The pseudo-first order rate constant observed for TCE degradation was essentially the same ($K_{obs} = 0.021 \text{ h}^{-1}$, $r^2 = 0.99$ for pH = 6.25 and $r^2 = 0.95$ for pH = 4.64). Maximum chloride formation (not shown) was also observed to be the same. When the initial pH was 4.64, the system adjusted itself to higher pH very quickly and then it followed the same behavior as with the initial pH 6.25. Thus, initial pH had an insignificant effect on the TCE degradation rate and chloride formation in the range of pH 4.6–6.25. At low pH values (< 5), H_2 production would be significant.

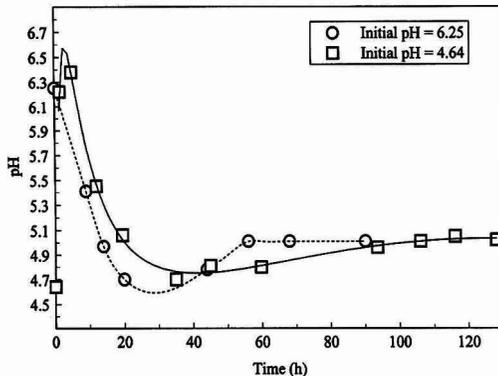
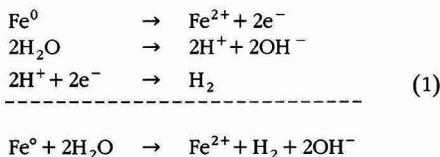


FIGURE 4 A typical pH of the solution vs. time plot obtained in batch experiments. Initial conditions: TCE = 80 mg/L, Iron = 250 gm/L

Reaction Scheme

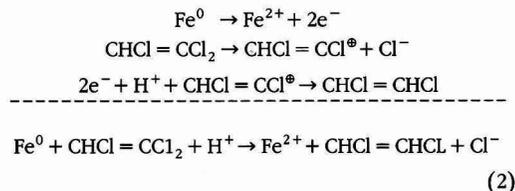
The reactions being considered here involve electron transfer and there are two potential electron acceptors here, water and organic molecules [6]. The possible reactions taking place then are:

- I) Metal Dissolution: (causes pH increase)

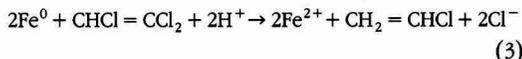


- II) Reduction of Trichloroethylene:

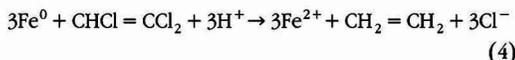
- I) For Dichloroethylene isomers:



- II) For Vinyl Chloride:



- III) For Ethene (complete dechlorination):



All these reactions take place simultaneously and there is a competition between the organic molecule and water for accepting the electrons released to the solution. It is known that the rate of dissociation of water by dissolution of iron (Reaction 1), is quite fast at low pH values. Conse-

quently, as the pH continues to drop (below 5.0) during the reaction, the dissociation of water may affect the overall extent of the reductive dehalogenation. In order to minimize the effect of competing reactions between TCE and H₂O, excess iron (molar ratio of Fe/TCE = 40 to 800) was used in all experiments. Experiments carried out at lower initial pH however show an insignificant effect on the degradation process, the final maximum chloride formation being the same.

The maximum chloride formation observed was about 75% even at 90% parent TCE degradation. The same maximum chloride formation was observed even after addition of fresh iron (Figure 2), and thus rules out the possibility of mass transfer limitation on further chloride formation due to the formation of precipitates on the iron surface. This means that either TCE is getting dechlorinated to some other products which are difficult to degrade or the products formed do not remain in the solution and thus not available for further degradation. The possible products of the degradation are dichloroethylene (DCE) isomers, vinyl chloride and various hydrocarbons as found by Gillham et al. [6]. The maximum amount of these species in the solution correspond to less than 10% of parent TCE concentration [16]. All these compounds are very volatile. Headspace formed during the experiment and hence there is a possibility of these compounds ending up in the headspace and thereby not available for degradation in the solution phase. The total organic carbon analysis of the samples before and at the end of the experiment shows that the total carbon remaining in the solution decreases with time. However the total organic carbon found in the sample exceeds that corresponding to the amount of TCE remaining in the solution at that time. This further suggests the possibility of other organic compounds being present in the solution which might contain bound chlorine with them. Burris et al. [2], have reported the concentration-time profiles of various intermediates resulting from the reductive TCE dechlorination by Vitamin B₁₂. The formation of refractory cis-1,2-DCE results in incomplete dechlorination.

Role of Dissolved Iron

The amount of iron dissolved in the solution was higher for reactive vials than control vials (containing no TCE) at any particular time (Table 1). This can be explained as follows: The rate of dissolution of iron is highly dependent on the prevailing pH conditions. The pH in the reactive solutions dropped with the time, so more iron was found to be dissolved in the solution compared to the control vials where pH showed a gradual increase due to reaction (1). At the beginning of reaction, the pH of the solution was high and little amount of dissolved iron was found in the

TABLE 1. Comparison of Dissolved Iron in Control and Reactive Sample Vials

Time (h)	Dissolved Iron (mg/L) Control (no TCE)	Dissolved Iron (mg/L) Reactive (with TCE)
15	1.13	3.60
25	2.00	14.5
39	2.75	23.0
59	3.10	25.5

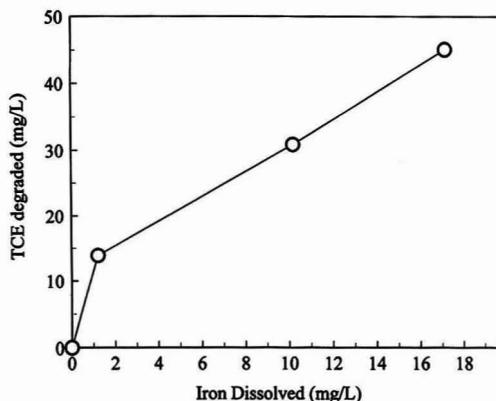


FIGURE 5 Relationship between the extent of TCE degradation and the amount of iron dissolution. Initial conditions: TCE = 80 mg/L, pH = 6.25

solution. However, in the same time period, a substantial amount of TCE was degraded. Therefore, the electrons released by iron would preferably go to TCE (reaction 2) than to water (reaction 1), leading to the higher destruction of TCE. But as the reaction progresses, the dissolution of iron by reaction (1), becomes dominant and consequently the rate of degradation of TCE was found to slow down. Thus, the amount of TCE being degraded at different time intervals is directly related to the amount of iron being dissolved. It was found that the amount of TCE that was degraded at a particular time, was directly proportional to the amount of iron dissolved in the solution at that time. Figure 5 shows that there was more degradation of TCE per unit amount of iron dissolved initially than later. Dissolved oxygen may play an important role in this process. High pH and oxygen levels exist in the solution at the start of reaction and dissolved iron will be in the form of Fe³⁺. Dissolved Fe³⁺ gives an additional electron compared to Fe²⁺ and the reduction process should be more rapid. Moreover, as the dissociation of water by reaction (1) is slow at higher pH, reaction (2) is favored and correspondingly we observe more degradation. As the reaction progressed, the amount of dissolved oxygen in the solution decreased as did the pH. At this condition iron in the solution would mainly be in the form of Fe²⁺, reaction (1) would be preferred and we observed less amount of TCE being degraded per mole of iron dissolved. The role of Fe²⁺/Fe³⁺ on the degradation process needs to be investigated in further detail.

Surface Area of Iron

Two different approaches were taken to study the effect of surface area on the reaction rate. In the first one, iron (100 mesh) loading in the reaction mixture was varied all the way from 25 gm/L to 500 gm/L (corresponding to surface area per unit volume of solution (S/V) ratio of 128 m⁻¹ and 2720 m⁻¹ respectively) to study its effect on the degradation rate. The observed rate constant, K_{obs}, was linearly proportional to the S/V ratio for S/V ratios < 1000 m⁻¹. Above S/V = 1000 m⁻¹, the rate constant was found to be independent of S/V (Figure 6). In the second approach, the same effect was studied by changing the particle size of iron at a particular loading. Here, experiments

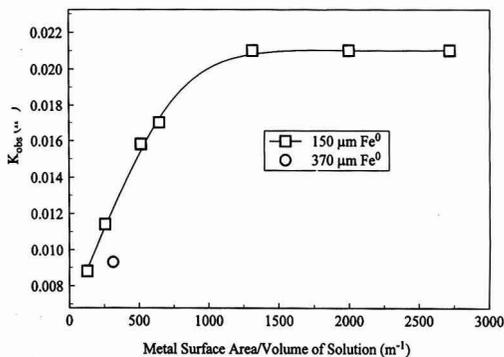


FIGURE 6 Effect of surface area per unit volume of solution (S/V) on observed TCE degradation rate constant. Initial conditions: TCE = 80 mg/L, pH = 6.25

were repeated for iron samples of 40 mesh and 100 mesh. The TCE degradation rate constants obtained by linear regression were as follows: 0.0093 h⁻¹ for 370 μm iron particle (r² = 0.99) and 0.021 h⁻¹ for 150 μm iron particle (r² = 0.99). Thus, approximately two fold increase in the rate constant was observed, when the particle size was increased from 370 μm (corresponding to S/V ratio of 43 m⁻¹) to 150 μm. This value also falls close to the linear region as can be seen from Figure 6. The chloride formation observed was also higher for lower particle size (Figure 7).

Reactions (1 - 4) depend on an active zero-valent iron surface. The ratio of the surface area of the metal to the solution volume (S/V) is a very important parameter in the degradation if the process rate is limited by the reaction. When the S/V ratio was varied by changing the iron loading in the solution, the apparent observed rate constant (K_{obs}) was found to increase linearly with the S/V ratio at lower S/V values (Figure 6). However, at higher S/V ratios, the rate constant was found to be independent of the same. This could be attributed to the fact that iron is very much in excess of the stoichiometric requirement and hence we observe the pseudo first order nature of the reac-

tion. Thus, at lower S/V ratios, mass transfer in the bulk solution controls the reaction and hence would be influenced by the type of mixing procedure adopted. At S/V ≥ 1310 m⁻¹ (corresponding to iron loading of 250 gm/L) K_{obs} was independent of S/V and would be kinetically controlled. Same effect was observed when experiments were carried out with different particle size for the same iron loading. The results show remarkable difference in both the chloride formation and TCE dechlorination rate, for two different mesh size iron samples. The rate of dechlorination was much faster with 150 μm iron particles than with 370 μm iron particles. This is consistent with the findings of Sivavec et al. [18], who have developed a linear correlation between the observed rate constant and the iron surface area per unit volume of solution, for commercial iron. The rate constant was directly proportional to the S/V of the solution. The rate constant for the higher particle size (corresponding to the lower surface area), falls close to the linear region in the graph (Figure 6), again emphasizing the need for higher surface area. Hence in order to have higher rates of dechlorination, one should look at different ways to achieve high surface area. One way to achieve this is using lower particle size, but one cannot go to very low particle size as then the contamination of iron surface by oxide coating may become very important factor and particle agglomeration should be taken into account. Other means to achieve high surface areas, for example, electroplating iron on inert fiber surface, using nanocrystalline iron particles are currently under consideration.

Proposed Mechanism

From the reaction scheme shown earlier, there are three possible reductants here: zero-valent iron, dissolved iron and hydrogen gas released during dissociation of water. Thus, the reductive dechlorination observed in the process can occur by one of following three processes [4]:

1. direct electrolytic reduction at the metal surface,
2. reduction by hydrogen produced during the corrosion process, or,
3. reduction by dissolved ferrous iron that is also produced by the corrosion process.

Based on the results obtained so far, it appears as if the first mechanism is prevalent. The dependence of the rate constant on the surface area of the metal is also consistent with mechanism 1. One can extend the analysis of Boronina et al. [2], to get an idea about the mechanism of reaction and is shown in Figure 8. According to this, TCE can first oxidatively add to Fe forming a reactive intermediate CHClFeCl₂. Due to the strong ionic nature of the Fe-Cl bond, this particular intermediate can undergo rapid protonation by water forming dichloroethylene isomers. Similarly, these dichloroethylene isomers can yield vinyl chloride and ultimately ethene. The hydroxyl ferrous compound formed during protonation of the reactive intermediate may further get protonated to form FeO, FeCl₂, Fe(OH)₂, Fe(OH)₃, etc., (depending on pH conditions) and HCl. The HCl thus formed accounts for the slight decrease in the pH obtained during the course of the reaction.

Orth et al. [17], have suggested the possibility of precipitous transfer of electrons to the TCE molecule so that the molecule doesn't leave the iron surface until it is completely dechlorinated to ethene. We can see that due to the excess amount of iron used with respect to its stoichiomet-

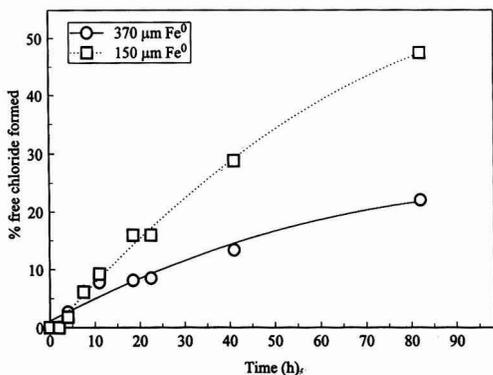


FIGURE 7 Effect of iron particle size on chloride formation. Initial conditions: TCE = 80 mg/L, pH = 6.25, Iron = 250 gm/L

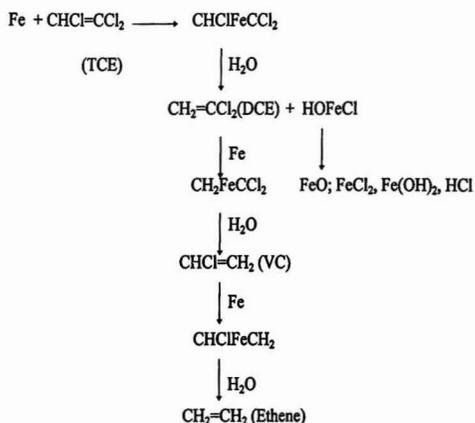


FIGURE 8 Proposed reaction mechanism (adapted from Boronina et al. [2])

ric requirement, there is no scarcity of the reactive sites on the metal surface for the organic molecule to form the intermediate reactive complex.

SUMMARY AND CONCLUSIONS

The rate of degradation of trichloroethylene was found to be independent of the initial TCE concentrations in the 72-103 mg/L range studied. Initial pH had an insignificant effect on the rate of degradation and chloride formation in the pH range studied (4.6-6.2). Presence of dissolved oxygen in the solution caused the lag period for chloride formation but the TCE degradation rate constant remained same. The maximum chloride formation observed was just 57% of the parent compound. The amount of TCE being degraded was directly proportional to the amount of dissolved iron in the solution at any given time. Surface area of the metal is very important parameter in the degradation process. At lower surface area to volume (S/V) ratios, the rate varied linearly with former, whereas at higher S/V ratios, the degradation process was found to be independent of the same. The reaction mechanism thus appears to be direct electrolytic reduction at the metal surface. Consequently, the particle size affects both the chloride formation and the rate of dechlorination. A two fold increase in the reaction rate was obtained with 2.5 fold decrease in the particle size of iron, indicating that the reaction rate is highly dependent on the metal surface area under consideration. The reaction appears to be pseudo first order with respect to the TCE considering the fact that the amount of iron used (10 gm in 40 ml, i.e., 250 g/L) is very much in excess of the stoichiometric requirement. The pseudo first order rate constant obtained under these conditions is 0.021 h^{-1} .

ACKNOWLEDGMENT

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LITERATURE CITED

1. Agrawal, A., L. Liang, and P. G. Tratnyek, "Phenomena Affecting Remediation of Organic Groundwater Contaminants with Iron Metal at Solid-Water Interface," American Chemical Society Extended Abstract, Industrial and Engineering Chemistry Division, p54 (September 17-20, 1995).
2. Boronina, T., K. J. Klabunde, and G. Sergeev, "Destruction of Organohalides in Water Using Metal Particles: Carbon Tetrachloride/Water Reactions with Magnesium, Tin, and Zinc," *Environ. Sci. Technol.*, **29**(6), pp. 1511-1517 (1995).
3. Burris, D. R., C. A. Delcomyn, M. H. Smith, and A. L. Roberts, "Reductive Dechlorination of Tetrachloroethylene and Trichloroethylene Catalyzed by Vitamin B₁₂ in Homogeneous and Heterogeneous Systems," *Environ. Sci. Technol.*, **30**(10), pp. 3047-3052 (1996).
4. Chuang, Fei-Wen, R. A. Larson, and M. S. Wessman, "Zero-Valent Iron Promoted Dechlorination of Polychlorinated Biphenyls," *Environ. Sci. Technol.*, **29**(9), pp. 2460-2463 (1995).
5. Freedman, D. L., and J. M. Gosset, "Biological Reductive Dechlorination of Tetrachloroethylene and Trichloroethylene to Ethylene Under Metagenic Conditions," *Appl. Environ. Micro.*, Vol. 55, pp. 2144-2151 (1989).
6. Gillham, R. W., and S. F. O'Hannesin, "Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron," *Ground Water*, **32**(4), pp. 958-967 (1994).
7. Glaze, W. H., and Joon-wun Kang, "Advanced Oxidation Processes for Treating Groundwater Contaminated with TCE and PCE: Laboratory Studies," *Journal AWWA*, May, pp. 57-63 (1988).
8. Gross, R. L., and S. G. Termath, "Packed Tower Aeration Strips TCE from Groundwater," *Environ. Prog.* **4**, pp. 119-124 (1985).
9. Hopkins, G. L., L. Semprini, and P. L. McCarty, "Microcosm and In-situ Field Studies of Biotransformation of Trichloroethylene by Phenol Utilizing Microorganisms," *Appl. Environ. Micro.*, **59**(7), pp. 2277-2285 (1993).
10. Korte, N. E., L. Grittini, R. Muftikian, Q. Fernando, L. Liang, and J. Clausen, "The Use of Paladized Iron as a Means of Treating Chlorinated Contaminants," American Chemical Society Extended Abstract, Industrial and Engineering Chemistry Division, pp. 51-53, September 17-20, 1995.
11. Liang, L., and J. D. Goodlaxson, "Kinetics and Byproducts of Reductive Dechlorination of Ground Water TCE with Zero-Valence Iron," American Chemical Society Extended Abstract, Industrial and Engineering Chemistry Division, pp. 46-49, September 17-20, 1995.
12. MacKenzie, P. D., S. S. Baghel, G. R. Eykholt, and D. P. Horney, J. J. Salvo, and T. M. Sivavec, "Pilot-Scale Demonstration of Chlorinated Ethene Reduction by Iron Metal: Factors Affecting Iron Lifetime," American Chemical Society Extended Abstract, Industrial and Engineering Chemistry Division, pp. 59-62, September 17-20, 1995.

13. **Matheson, L. J., and P. G. Tratneyk**, "Reductive Dehalogenation of Chlorinated Methanes by Iron Metal," *Environ. Sci. Technol.*, **28**(6), pp. 2045-2053 (1994).
14. **McKinnon, R. J., and J. E. Dyksen**, "Removing Organics from Groundwater through Aeration Plus GAC," *Journal AWWA*, pp. 42-47 (1984).
15. **Nelson, Michael J. K., S. O. Montgomery, W. R. Mahaffey, and P. H. Prtichard**, "Biodegradation of Trichloroethylene and Involvement of an Aromatic Biodegradative Pathway," *Appl. Environ. Micro.* **53**(5), pp. 949-954 (1987).
16. **O'Hannesin, S. F., R. W. Gillham, and J. L. Vogan**, "TCE Degradation in Groundwater Using Zero-Valent Iron," American Chemical Society Extended Abstract, Industrial and Engineering Chemistry Division, pp. 55-58, September 17-20, 1995.
17. **Orth, W. S. and R. W. Gillham**, "Dechlorination of Trichloroethylene in Aqueous Solution Using Fe⁰," *Environ. Sci. Technol.*, **30**(1), pp. 66(1996).
18. **Sivavec, T. M., D. P. Horney, and S. S. Baghel**, "Reductive Dechlorination of Chlorinated Ethenes by Iron Metal and Iron Sulfide Minerals," American Chemical Society Extended Abstract, Industrial and Engineering Chemistry Division," pp. 42-45, September 17-20, 1995.
19. **Vogel, T. M., and P. L. McCarty**, "Biotransformation of Tetrachloroethylene, Dichloroethylene, Vinyl Chloride and Carbon Dioxide under Methanogenic Conditions," *Appl. Environ. Micro.*, **49**(5), pp. 1080-1083 (1985).
20. **Wilson, J. T., and B. H. Wilson**, "Biotransformation of Trichloroethylene in Soil," *Appl. Environ. Micro.*, **49**(1), 1985, pp. 242-243.

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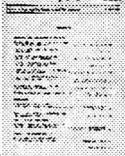
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