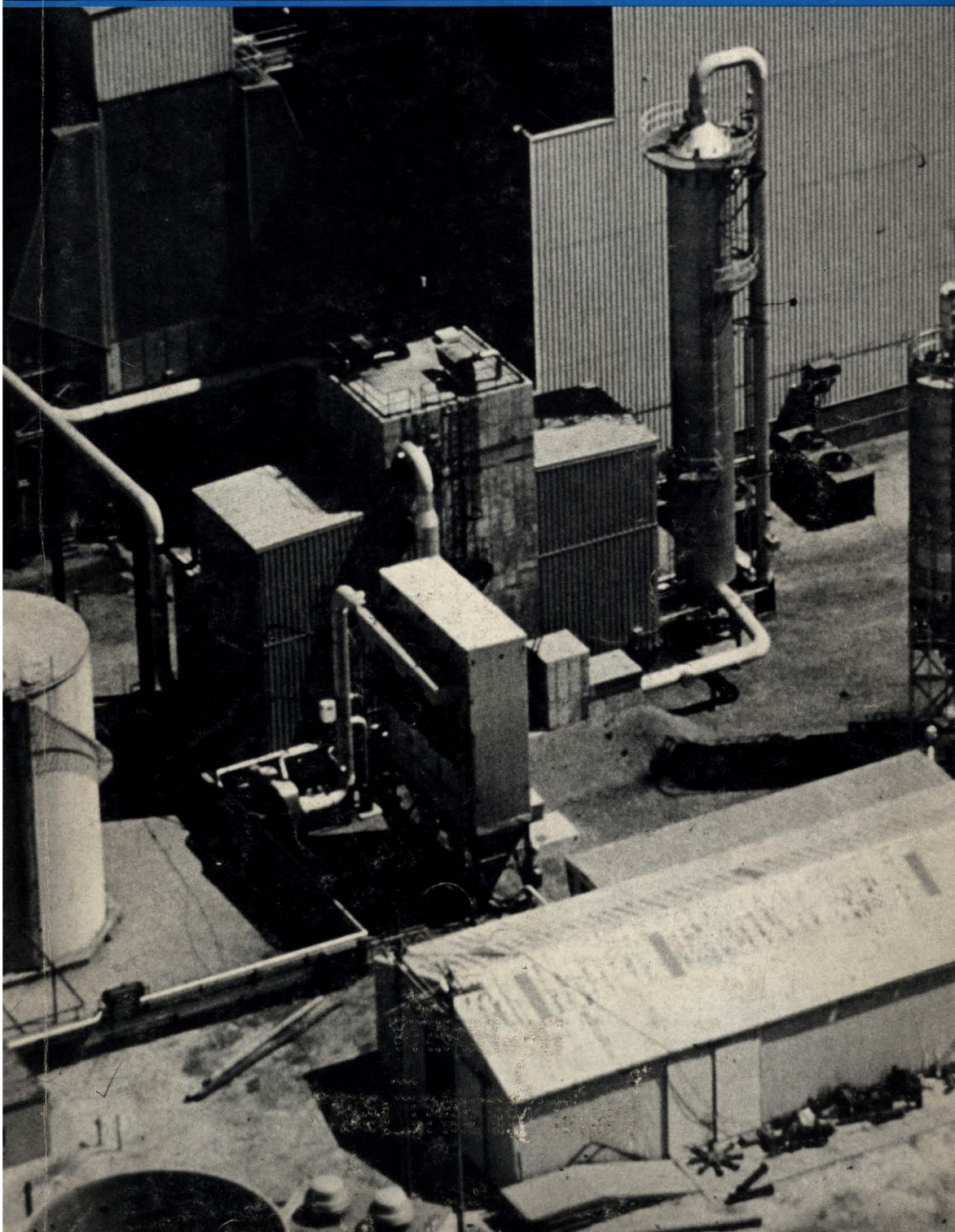


AUGUST 1987

# ENVIRONMENTAL PROGRESS



THE CENTER FOR CHEMICAL PROCESS SAFETY presents



# GUIDELINES for Hazard Evaluation Procedures

In 1985 AIChE established the *Center for Chemical Process Safety (CCPS)* which will utilize the expertise of chemical engineers to develop recommendations and guidelines for acceptable industry practices in the production, storage and handling of toxic or reactive chemical materials.



The Center's first publication, *Guidelines for Hazard Evaluation Procedures* concentrates on hazards involving the release of flammable, combustible, highly reactive, or toxic materials in amounts sufficient to endanger the health and safety of chemical plant employees and the neighboring public. The 200-page volume, which is being published in loose-leaf form (with binder) for easy updating, also details procedures for predicting potential hazards through systematic, element-by-element examination of a process or plant.

ISBN 0-8169-0347-6  
Pub. No. G-1

AIChE Members: \$35  
Others: \$75

**SEND ORDERS TO:** Publications Sales Dept. P, American Institute of Chemical Engineers, 345 E. 47 St., New York, NY 10017. All orders must be prepaid. No charge for postage or handling on U.S. orders. All foreign orders must be accompanied by payment in U.S. dollars and must include \$2.00 per book to cover postage and handling. All books will be shipped bookrate. All sales are final. (*Prices are subject to change.*)

Prepared by  
Battelle Columbus Division  
for the  
American Institute of Chemical Engineers

# ENVIRONMENTAL PROGRESS

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

Publisher  
Diane Foster

Editor  
Gary F. Bennett  
(419) 537-2520

Managing Editor  
Maura Mullen  
(212) 705-7327

Editorial Assistant  
Karen M. Simpson

Production Assistant  
Jeanne M. McQuade

#### Editorial Review Board

D. Bhattacharyya  
R. Lee Byers  
S. L. Daniels  
T. H. Goodgame  
Stephen C. James  
Atly Jefcoat  
William J. Lacy  
P. Lederman  
R. Mahalingham  
Robert W. Peters  
C. J. Touhill  
Andrew Benedek  
J. A. Scher  
Leigh Short  
R. Siegel  
Andrew Turner  
Wei-Chi Ying

Publication Office, 215 Canal Street, Manchester, N.H.  
Published quarterly by the American Institute of Chemical Engineers, 345 East 47 St., New York, N.Y. 10017. (ISSN 0278-4491). Manuscripts should be submitted to the Manuscript Center, American Institute of Chemical Engineers, 345 East 47 St., New York, N.Y. 10017. Statements and opinions in *Environmental Progress* are those of the contributors, and the American Institute of Chemical Engineers assumes no responsibility for them. Subscription price per year: \$50. Outside the U.S. please add \$5 per subscription for postage and handling. Single copies \$18. Outside the U.S. please add \$2 for postage and handling. Payment must be made in U.S. dollars. Second-class postage paid at New York, N.Y. and additional mailing offices. Copyright 1987 by the American Institute of Chemical Engineers.

Volume 6

Contents

Number 3

#### Editorial

*Michael R. Overcash* ..... A2

#### From the Editor

*Gary F. Bennett* ..... A5

**Environmental Shorts** ..... A6

**Books** ..... A7

**Washington Environmental Newsletter** ..... A8

**Environmental Division Programs  
(AIChE Annual Meeting, New York)** ..... A9

**Recommendations for the Regulation of Air Toxics**  
*Jacoby A. Scher (principal author)* ..... A12

**Membrane Utilization in Hazardous Metal Removal  
from Wastewater in the Electronic Industry**  
*Shmuel Sternberg* ..... 139

**Removal of Heavy Metals in Wastewater in a Clay Soil  
Matrix Using Electro-Osmosis**  
*Chittaranjan Ray and R. H. Ramsey* ..... 145

**Adsorption of Inorganic Arsenic and Organoarsenicals  
on Hazardous Oxides**  
*Mriganka M. Ghosh and Jill R. Yuan* ..... 150

**Rapid Renovation of a Sludge Lagoon**  
*E. A. Dienemann, J. F. Magee II, D. S. Kosson and R. C. Ahlert* ..... 158

**Feasibility of Intermittent Biological Treatment for Hazardous Wastes**  
*A. Scott Weber and Mark R. Matsumoto* ..... 166

**Destruction of Volatile Organic Compounds via Catalytic Incineration**  
*Bruce A. Tichenor and Michael A. Palazzolo* ..... 172

**Operating and Testing a Combined SO<sub>2</sub> and NO<sub>x</sub> Removal Facility**  
*Norman W. Frank, Gary A. Miller, and David A. Reed* ..... 177

**H<sub>2</sub>S/SO<sub>2</sub> Removal in the Modified-Claus Reaction  
Over Packed Alumina Beds**  
*C.-L. (Joe) Chou* ..... 183

**Controlling Acid Deposition by Seasonal Gas Substitution  
in Coal-and-Oil Fired Power Plants**  
*Gary Galeucia, Dan Golomb, and James A. Fay* ..... 190

**Fluid Flow and Gas Absorption in an Ejector Venturi Scrubber**  
*Iclal Atay, Gordon Lewandowski and Richard Trattner* ..... 198

**Cover: Process demonstration unit (see article on page 177).  
Photo courtesy Ebara International Corporation, Greensburg, PA.**

Reproducing copies: The appearance of the code at the bottom of this page indicates the copyright owner's consent that for a stated fee copies of articles in this journal may be made for personal or internal use or for the personal or internal use of specific clients. This consent is given on the condition that the copier pay the per-copy fee (appearing as part of the code) through the Copyright Clearance Center, Inc., 21 Congress St., Salem, Mass. 01970 for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to copying for general distribution, for advertising or promotional purposes, for inclusion in a publication, or for resale.  
*Environmental Progress* fee code: 0278-4491/87 \$2.00. Postmaster: Please send change of addresses to *Environmental Progress*, AIChE, 345 East 47 Street, New York, N.Y. 10017.

# Two Primary Environmental Challenges for Industry and Engineering (1987-1997)

**Michael R. Overcash**

As the chemical engineering society examines the future of our profession, the environment (along with safety and health) is identified as one of seven major challenges according to a major National Academy of Science study. This editorial is part of an effort to specifically define which issues in the environment are the major challenges to Chemical Engineering. Certainly there are equally important problems, but the two issues identified here are probably the most profound, and will directly utilize the most resources as we respond to the past and look to the future of air, water, and terrestrial resources.

The future efforts of industry and academic personnel in the area of waste reduction or elimination is one of two major frontiers in the environmental field. In capsule, there will be a transition in the magnitude and environmental impact (toxicity and fate) of wastes or emissions from all industry which parallel the profound changes in the pesticide manufacturing field. The pesticide or agricultural chemicals field converted, over a decade, from highly chlorinated, persistent materials to more degradable, direct acting chemicals, and now toward greatly reduced, integrated pest management. This is a substantive change which when transferred to all manufacturing industrial categories demonstrates the magnitude of this national transition. For the rest of industry, the cost of discharge (to streams, atmospheric, or hazardous wastes) will continue to rise as attention is focused on chemicals which at low chronic levels pose health and environmental concern. The rise in environmental costs (whether direct charges or indirect perceptions of liability) will be the driving force for such transitions, while the time-frame for significant reduction is probably one to two decades. That is, if one were to compare the percentage of wastes and specific chemicals of concern generated which are presently discharged to the environment (landfills, atmospheric emissions, or effluents to receiving waters) it will be shifted from 80%-100% to <20% as the scientific personnel pursue the goals of waste reduction. These will be major changes and hence pose the challenges for chemical engineering research.

There is a more profound research challenge to the chemical engineering profession than the simple acceptance of goals to substantively reduce environmental emissions. That challenge is to play a major role in determining how clean a discharge or how much reduction must be established as the objective. If we as a profession are to avoid a cycle in pursuit of zero we must contribute substantively to the decisions on the reasonable levels of environmental discharge. The latter environmental frontier is inherently tied to the successes in economic waste reduction, but is a separate area of research. The success in contributing to the "how clean is clean" engineering challenge centers on actual experimental investments as opposed to theoretical advances. That is, major weight is given to actual data on exposure, fate, background levels, feasibility of control, etc. Thus as chemical engineers in industry, government, or universities this will be a two directional challenge to us to both reduce, on a major scale, waste generation to all environmental media and to establish the appropriate environmental endpoints which achieve acceptable risk.

In the past decade the regulatory framework has moved constantly toward greater control of environmental discharge. The industrial response has been largely one of waste treatment and transfer to solid waste for landfills. Thus the past intellectual accomplishments and response to societal needs have been few since the pressure has been on regulatory concepts. The next decade poses major challenges since a number of the uncontrolled practices of society have become subject

---

to regulatory scrutiny. The new frontiers are to greatly reduce the levels of constituents which are often already present at low levels. In addition, everyone is sensitive to the fact that standards for human exposure or for the environment can be arbitrary and often are set in the absence of much quantitative information. Thus the demonstration of process modifications or recovery technologies needs to move much further ahead so that end-of-pipe treatments are not the only solutions. In addition the technical community must undertake the quantification studies for the range of issues raised in the setting of environmental standards or endpoints.

Several incentives and activities have been aimed at this environmental frontier. The AIChE Environmental Division (ED) has restructured to specifically focus on waste reduction in two principal subcategories of approach. These are process modification and recycle/recovery technologies. The ED has a significant number of technical sessions and a part of the Hazardous Waste Management Continuing Education course is devoted to the broad industrial approaches for waste minimization. In addition, the ED has a major technical session commitment in the area of fundamental environmental research and hence toward the issues of environmental standards. The National Academy of Science has recently completed a study to identify the barriers to hazardous waste reduction, which further signals identification of this area as a priority frontier.

The second major frontier in the environmental field is centered on the means by which society can clean up the legacy which we are discovering at the present time. This frontier is as critical in providing solutions for past practices and mistakes as the pollution prevention frontier is critical in reducing the likelihood of generating a legacy today for future generations.

Importance of innovative means of detecting and providing remedies in this area is illustrated by economics. The clean up cost of single site, such as an abandoned landfill or underground contamination of water resources is conservatively between one and ten million dollars. The number of sites from the EPA priority list, the Department of Defense locations, and prudent estimates of secondary priorities or undiscovered situations is between one and five thousand. This yields financial implications between \$1 billion and \$50 billion. It is this stage, on which the intellectual and societal challenges for the renovation of past practices is set. It is this stage which poses substantive challenges for chemical engineers and industry.

Research needs exist across the entire range of issues that arise in this field. As examples one can cite as research needs for groundwater and industrial sites, detection of contamination, rate of expansion of pollution, interaction of chemicals with the environment, treatment *in situ*, other forms of treatment, and monitoring of progress. All of these have substantial chemical and mechanistic characteristics such as kinetics, multi-phase equilibria, diffusion, etc. which require experimental and theoretical explorations. The need for innovation and a strong understanding of which remedial actions will lead to the required end points is paramount when such large financial consequences are involved. In addition, the past practices of industry have largely led to the present situation and chemical engineers are an integral part of past and future industrial prosperity, and thus this environmental issue would appear to be a central challenge to our profession.

The past chemical engineering advances are largely unquantified since the impetus to undertake clean-up is just emerging. As with the field of preventing waste emissions, the remedial situation will be highly sensitive to the standards established for acceptable environmental levels. Thus chemical engineering needs exist in the science of setting clean-up criteria. The field of remedial strategies for past industrial practices contains a broad range of professional specialties with which chemical engineers would interact. These range from political and social scientists to basic scientists in physics and chemistry.

---

*Michael R. Overcash, Professor of Chemical Engineering at North Carolina State University, is currently an EPA Distinguished Scientist and a member of the North Carolina Governor's Waste Management Board. Overcash is a past chairman of the Environmental Division of the American Institute of Chemical Engineers. He has contributed to the understanding of environmental processes and the technology for major industrial reduction in the generation of toxic chemicals. Dr. Overcash has published eight books, over sixty journal articles and one hundred ten papers for Symposia Proceedings.*

# Publications from AIChE

## New AIChE Symposium Series Title

### **Electrochemical Engineering Applications**

*Ralph E. White, Robert F. Savinell & Alfred Schneider,  
Editors*

*(AIChE Symposium Series Volume 83, No. 254)*

This volume consists of papers presented at the AIChE Annual Meeting held in Miami Beach, November 2-7, 1986. They relate to fundamental electrochemistry and industrial electrochemical processes, and report advances being made in applying engineering and scientific principles to understanding industrial electrolytic systems.

#### **PARTIAL CONTENTS**

Kinetics of Copper Dissolution at Oxygen Free and Phosphorized Anodes. Corrosion of Zinc by Bromine Under Flow Conditions. A Mathematical Model for the Photoelectrochemical Etching of Semiconductors. Catalytic and Electrocatalytic Oxidation of Methane Polarization of Silver Electrodes. Surface Diffusion Limited Oxygen Exchange in Zirconia Electrochemical Cells. Phenomenological Discharge Voltage Model for Lead-Acid Batteries. Simulation of a Rechargeable Hydrogen-Bromine SPE Cell. Numerical Analysis on Shunt Current and Pumping Loss in a Redox-Flow Cell System. Electrochemical Process for Dissolving Plutonium Dioxide and Leaching Plutonium from Scrap or Wastes. The Application of Electrorefining for Recovery and Purification of Fuel Discharged from the Integral Fast Reactor. Electropolishing Applications in the Nuclear Industry.

1987 160 pp. ISBN 0-8169-0405-7 LC87-11555

Pub S-254 AIChE Members \$20 Others \$40

## New Publications From the Center for Chemical Process Safety

### **Guidelines for Vapor Cloud Dispersion Models**

*Steven R. Hanna & Peter J. Drivas*

The dynamic field of modeling episodic releases of hazardous or toxic materials is made accessible in this book. Developed from the current reports and manuscripts of researchers and model developers, it is the state-of-the-art. This practical and concise resource of great value to the beginner, the expert, and the manager promotes understanding of the uses and limitations of this advanced tool. This is a publication of the Center for Chemical Process Safety.

#### **CONTENTS**

Conclusions and Recommendations. Introduction. Overview of Release Scenarios and Modeling Procedures. Source Emission

Models. Transport and Dispersion Models. Model Evaluation Experience and Uncertainties Estimates. References. Nomenclature. Index. Appendix A: Summary of Operational Models. Appendix B: Examples of Hazardous Chemical Release Scenarios.

1987 176 pp. est. ISBN 0-8196-0403-0 LC87-1166

Pub G-2 AIChE Members \$40 Others \$75

### **Proceedings of the International Symposium on Preventing Major Chemical Accidents**

*Sponsored by The Center for Chemical Process Safety of the  
American Institute of Chemical Engineers, The U.S.  
Environmental Protection Agency & The World Bank.*

The papers presented at this symposium held in Washington D.C. on February 3-5, 1987 contain the latest information as it was presented by world experts. Topics covered range from quantitative risk analysis to human error considerations.

#### **PARTIAL CONTENTS**

Mathematical Models for Atmospheric Dispersion of Hazardous Chemical Gas Releases. Reduction of Risks by Reduction of Toxic Material Inventories. Safety Policy for the Rijnmond Region. Concrete in Chemical Plants. Safety Considerations in the Design of Batch Processing Plants. Relief System Design for Run-away Chemical Reactions. Reactive Chemical Hazards. Calorimetric Methods Used in the Assessment of Thermally Unstable or Reactive Chemicals. Post-Release Mitigation Design for Mitigation of Releases. Hazard Control Methods of High Volatility Chemicals. Remote Sensing of Fire and Hazardous Gases. The Potential of Aqueous Foams to Mitigate the Vapor Hazard from Released Volatile Chemicals. Approaches to the Control of the Effects of Human Error on Chemical Plant Safety. Ensuring Operator Reliability During Off-Normal Conditions Using an Expert System. A Methodology for Chemical Hazards Analysis at Nuclear Fuels Reprocessing Plants. Relative Advantages of People and Machines in Process Industries.

1986 500 pp. est. ISBN 0-8169-0411-1 LC87-12642

Pub P-47 AIChE Members \$40 Others \$75

**SEND SUBSCRIPTIONS to:** AIChE Subscriptions Dept. C, 345 East 47 Street New York NY 10017.

**SEND BOOK ORDERS to:** AIChE Publication Sales Dept. C, 345 East 47 Street New York NY 10017.

Specify title and Pub.# of book. Members may order only one copy at the discounted price and must supply their Membership ID# and countersign the purchase order. **Enclose check or money order with all orders.** No charge for postage or handling on prepaid U.S. surface/bookrate shipments. All foreign orders must be prepaid in U.S. dollars (check, money order or international bank draft drawn on a N.Y. bank) and must include \$6.00 per book (unless otherwise specified) to cover postage & handling on surface/bookrate shipments. When faster service is required, contact AIChE to determine extra cost. Allow 4 weeks for delivery in U.S. and Canada.

*Prices subject to change. All sales are final.*

## **Environmental Progress Readership Survey**

At a meeting of the *Environmental Progress* Editorial Advisory Board held in Chicago in 1986, it was suggested that a readership survey be conducted. Subsequently a survey questionnaire designed by Robert Peters (Purdue) and Atty Jefcoat (Alabama) was published in the November 1986 issue.

Unfortunately the response to the survey was disappointing (1.85% or 62 responses from the 3,353 potential responses). I believe the reason for the poor return was because the questionnaire was quite lengthy (probably over-ambition on our part in order to obtain data) and was bound at the back of the issue, resulting in the survey being missed by most readers.

Although responses were not extensive, they were well thought-out and the information will be used to guide *Environmental Progress's* editor in his duties. Some of the guidance (data) is reported below:

- The respondents consisted of 26% consultants, 19% government, 15% professors, 13% plant operation, and 10% R&D.
- 75% are involved with hazardous waste and wastewaters; 50% are involved with all media; air water and solid waste.
- Regarding coverage: 25% of the readers thought more attention should be given to hazardous waste; 30% thought water should receive more coverage; many of the readers felt there was excessive emphasis on air pollution.
- 80% of the readership thought the technical level of articles was appropriate.
- *Environmental Progress* was rated well when compared with other technical environmental journals.
- The readers liked the ancillary features—editorial; environmental shorts; Washington Environmental Newsletter.
- Most of the readership felt *Environmental Progress* should feature lists of environmental meetings and entrée to research grant applications.
- Nearly 75% of the readership favored having special issues devoted to a particular topic.

The editor sincerely thanks Drs. Peters and Jefcoat for their work on the survey and analysis thereof, and also thanks those who took the time to fill out the questionnaire. The results are being used. The following recommendations have been implemented since receipt of the survey:

- More emphasis is being placed on hazardous waste.
- One special (single topic) issue has been published and another is planned for next year. If these issues are well received, one issue will be devoted to a single topic each year.
- A book review editor is being sought.

Suggestions and comments by readers are always welcome.

**Gary F. Bennett**  
*Editor*

## Environmental Shorts

### Superfund Handbook Now Available

ERT Inc., of Concord, Massachusetts, has announced the availability of a second edition of its *Superfund Handbook*. This second edition has been revised to cover the "new" Superfund program — the Superfund Amendments and Reauthorization Act (SARA) and the Emergency Planning and Community Right-to-Know Act (Title III).

Written in question and answer format, the Handbook takes readers step-by-step through the Superfund process detailing new and existing provisions. It helps readers formulate practical strategies for dealing with complex Superfund requirements, highlighting the important aspects of the new SARA and Title III programs. In addition, time and cost

savings tips are provided for complying with Superfund.

For a complimentary copy of the *Superfund Handbook* write on your business letterhead to ERT Inc., Marketing Department, 696 Virginia Road, Concord, Massachusetts 01742, or call ERT toll free at 1-800-722-2440. Large quantities of the Handbook may be purchased for \$9.00 each.

### New edition of *Who's Who in Environmental Engineering*

The 1987 edition of *Who's Who in Environmental Engineering*, published by the American Academy of Environmental Engineers, is now available.

The book provides a complete listing of environmental engineers in all occupation groups, such as, consulting, government, education, etc., who have proven to their peers through an extensive review and examination process that they have

special knowledge in one or more of the following areas: Air Pollution Control; General (Public Health) Environmental Engineering; Industrial Hygiene; Radiation Protection; Solid Waste Management and Water Supply and Wastewater Engineering.

Divided into three primary sections, the book lists environmental engineers alphabetically, by specialty and by geography (state or

foreign country). The book also describes in detail the certification program that each must satisfy to obtain this distinction along with historical and organizational data about the Academy.

Copies of the hardcover edition can be purchased for \$50 postage paid from the American Academy of Environmental Engineers, 132 Holiday Court, Annapolis, Maryland 21401.

### Puget Sound Acidity Levels Drop After ASARCO Shutdown

The levels of acidity in Puget Sound region rainfall have decreased significantly since the shutdown of the ASARCO copper smelter in Tacoma, Washington, according to a study funded by the U.S. Environmental Protection Agency.

The two-year study was managed by the U.S. Department of Energy's Pacific Northwest Laboratory and conducted in cooperation with the University of Washington. Battelle Memorial Institute oper-

ates PNL for DOE.

"Study results indicate that sulfate and hydrogen ion concentrations obtained from samples taken before the closure were significantly different than those collected after the shutdown," said Dr. Nels S. Laulainen of Battelle's Earth and Environmental Science Center. "In addition, rainwater samples collected downwind during smelter operation were also significantly different from those collected upwind.

"Sulfur dioxide is considered to

be one of the principal contributors to acid rain," explained Laulainen. "According to the Puget Sound Air Pollution Control Agency, the smelter was a major source of sulfur dioxide emissions in the Puget Sound region before it shut down in March 1985." Acid rain is suspected to cause fish loss in streams and lakes and is the alleged cause of other detrimental environmental effects including damage to forests and buildings.



# BOOKS

**Hazardous Communication: Issues and Implementation**, Brower, J. E., ed., ASTM, Philadelphia, PA, 1987, \$37.00, 213 pgs.

**Drum Handling Manual for Hazardous Waste Sites**, Wagner, K., Wetzel, R., Bryson, H., Furnam, C., Wickline, A., and Hodge, V., Noyes Data Corp., Park Ridge, NJ 1987, \$36.00, 177 pgs.

**Protection of Public Water Supplies from Ground-Water Contamination**, Pettyjohn, W. A., ed., Noyes Data Corp., Park Ridge, NJ 1987, \$36.00, 177 pgs.

**Guide to Safe Practices in Chemical Laboratories**, Royal Society of Chemists, London, U.K., 1987, \$18.00, 48 pgs.

**Decontamination Techniques for Buildings, Structures and Equipment**, Esposito, M. P., McCardle, J. L., Crone, A. H., Greber, J. S., Clark, R., Brown, S., Halowell, J. B., Langham, A., and McLardish, C. D., Noyes Data Corp., Park Ridge, NJ, 1987, \$34.00, 262 pgs.

**Underground Tank Leak Detection Methods**, Nikae, S., and Broccious, J. A., Noyes Data Corp., Park Ridge, NJ \$36.00, 123 pgs.

**Gaseous Detonations—Their Nature, Effects and Control**, Nettleton, M. A., Chapman and Hall, London, 1987, 255 pgs.

**Biotechnological Advances in Processing Municipal Wastes for Fuels and Chemicals**, Antonopoulos, A. A., ed., Noyes Publications, Park Ridge, NJ, 1987, \$45.00, 488 pgs.

**Air Pollution Control Technology**, Bretschneider, B., and Kurfurso, J. Elsevier, Amsterdam, 1987, \$75.50, 297 pgs.

**Lime For Environmental Use**, Guteschick, K. A., ASTM, Philadelphia, PA, 1987, \$29.00, 147 pgs.

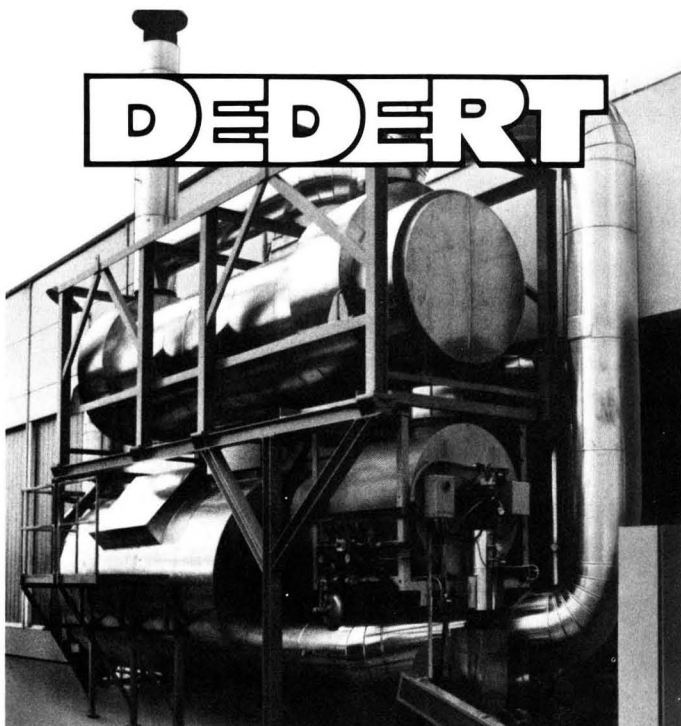
**Toxic Air Pollution: A Comprehensive Study of Non-Criteria Air Pollutants**, Liroy, P. J., and Daisey, J. M., Lewis Publishers, Chelsey, MI, 1987, \$44.95, 297 pgs.

**Hazardous and Industrial Solid Waste Testing and Disposal, Vol. 6**, Lorinzen, P., Conway, R. A., Jackson, L. P., Hamaza, A., Perket, C. L., and Lacy, W., ASTM, Philadelphia, PA, 1987, \$63.00, 471 pgs.

**Major Chemical Hazards**, Marshall, V. C., Ellis-Horwood, Chichester, UK, 1987, \$59.50, 587 pgs.

**Hazardous Waste Management Engineering**, Martin, E. J., and Johnson, J. H., Jr., eds., Van Nostrand Reinhold, New York, 1986, \$67.50, 520 pgs.

**Atmospheric Pollutions**, Pickett, E. E., ed., Hemisphere Publishers, New York, NY, 1987, \$62.50, 285 pgs.



## Dedert/Topsøe CATOX Catalytic Incineration

Dedert/Topsøe CATOX catalytic incinerators are extremely effective at removing volatile organic compounds from exhaust gases. The CATOX process is very reliable and uses a proprietary CK 302 metal oxide catalyst. The catalyst is resistant to poisoning by sulfur, chlorine and silicones, and has a guaranteed life of 12,000 hours, with 30,000 hour life expected in most applications. CATOX plants can be designed for autothermal operation in many cases, and can handle varying inlet concentration and flowrate without damage to the catalyst or the equipment. Some typical industrial applications for the CATOX system include: printing, plastics, tape and coatings manufacturers, phthalic anhydride, petrochemical, pharmaceutical, adhesives and production line painting operations.

Dedert Corporation, 20000 Governors Drive,  
Olympia Fields, Illinois 60461-1074 (312) 747-7000.

# D=DERT

# Washington Environmental Newsletter

## Biotechnology Regulation

There is increased concern both within EPA and Congress over the need to correctly characterize the environmental and health risks that our society must deal with. One area receiving an increased level of attention is the regulation of the products of biotechnology or "genetic engineering". EPA's Office of Toxic Substances (OTS) is primarily charged with this responsibility.

Recent advances in biological research are providing powerful new tools for altering the genetic makeup of plants, animals and micro-organisms and almost every company producing biological or chemical products is actively pursuing such R&D. A recent study predicted that by the year 2000, sales of biotechnology products could reach as high as \$40 billion a year; regulating this economically important industry in a manner that does not unduly impede innovation and progress while insuring the protection of human health and the environment is a major challenge now facing the Federal Government.

Under EPA's biotechnology policy, OTS has been given the responsibility for reviewing premanufacturing notices (PMN's) for the testing and use of "new" micro-organisms that have been manipulated to possess new traits. The authority for this review is the same as OTS authority to review new chemicals—Section 5 of the Toxic Substances Control Act (TSCA).

According to Charles L. Elkins of OTS, they are initially treating biotechnology PMN's involving environmental releases somewhat differently from other PMN's. For example, EPA's Biotechnology Science Advisory Committee, made up of experts from outside EPA, is actively involved in the evaluation of environmental releases. With this advisory help, OTS develops a risk assessment of the proposed product and reaches a regulatory decision. As with other PMN's, the decision could allow manufacture and use without restriction; to permit manufacture and use with specified restrictions; or to prohibit manufacture. EPA may also decide that there is insufficient information to evaluate potential risks and require that additional data be submitted.

In short, biotechnology R&D is already beginning to yield products which are subject to review in TSCA and thus subject to the procedures and safeguards that such reviews call for.

The Government Programs Steering Committee (GPSC) of AIChE is in the process of producing a "Commentary" on Biotechnology Regulation containing some recommendations that we hope will help biotechnology continue to become a new growth area without posing unreasonable risks to human health or the environment. As new biotech products come out of the R&D mode and into production, chemical engineers will have an increasingly important role.

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

# Environmental Division Programs

## (30 Sessions)

**AICHe Annual Meeting New York, NY November 15-20, 1987**

Dr. B. Mo Kim Group Coordinator  
General Electric Company  
Corporate Research and Development  
K-1 ESB 118  
Schenectady, N.Y. 12301  
(518) 387-6596

### AIR (11 Sessions)

Mr. Paul Shapiro Area Coordinator  
Office of Research and Development (RD-681)  
U.S. EPA  
401 M St., SW  
Washington, DC 20460  
(202) 382-2583

#### 1. Fundamentals of Aerosol Behavior

Dr. John Seinfeld (Chairman)  
Department of Chemical Engineering  
California Institute of Technology  
Pasadena, CA 91125  
(818) 356-6811

Dr. E. James Davis (Co-Chairman)  
Department of Chemical Engineering  
University of Washington  
Seattle, WA 98195

#### 2. Toxic Vapor Cloud Dispersion

Dr. Michael T. Mills (Chairman)  
ERT  
696 Virginia Road  
Concord, MA 01742  
(617) 369-8910

Dr. Francis Binkowski (Co-Chairman)  
U.S. EPA  
Atmospheric Sciences Research Laboratory  
MD-80  
Research Triangle Park, NC 27711

#### 3. Indoor Air Pollution

Bruce Tichenor (Chairman)  
U.S. EPA  
Air and Energy Engineering Research Laboratory  
MD-54  
Research Triangle Park, NC 27711

#### 4. Thermal Conversion of Municipal Sludge

Dr. Harry Bostian (Chairman)  
U.S. EPA  
Water Engineering Research Laboratory  
Cincinnati, OH 45268  
(513) 569-7619

Dr. Paul F. Fennelly (Co-Chairman)  
Air Toxics Engineering and Monitoring  
ERT  
696 Virginia Rd.  
Concord, Mass. 01742  
(617) 369-8910 X-560

#### 5. Thermal Conversion of Municipal Solid Waste

James D. Kilgroe (Chairman)  
U.S. EPA  
Air and Energy Engineering Research Laboratory  
MD-65  
Research Triangle Park, NC 27711  
(919) 541-2854

Dr. Joseph R. Visali  
NYSERDA  
2 Rockefeller Plaza  
Albany, N.Y. 12223

#### 6. Acid Rain Control—DOE's Clean Coal Program

Gregory C. Ondich (Chairman)  
Office of Research and Development (RD-681)  
U.S. EPA  
401 M Street, S.W.  
Washington, DC 20460  
(202) 382-2583

#### 7. Control of Hydrogen Sulfide from Hot Coal Derived Gas Streams

Dr. George R. Gavalas (Chairman)  
Department of Chemical Engineering  
California Institute of Technology  
Pasadena, CA 91125  
(818) 356-4152

Dr. B. M. Kim (Co-Chairman)  
Corporate Research and Development  
General Electric Company  
K-1, ESB 118  
Schenectady, NY 12301  
(518) 387-6596

#### 8. Innovative and Cost Effective Emission Control Technologies

Dr. Robert E. Kenson (Chairman)  
Systems Division  
Met-Pro Corporation  
160 Cassell Road  
Box 144  
Harleysville, PA 19438  
(215) 723-6751  
Marshall Dick (Co-Chairman)  
Office of Research and Development (RD-681)  
U.S. EPA  
401 M Street, S.W.  
Washington, DC 20460

#### 9. Characterization of Air Toxic Emissions from Industrial Chemical Facilities—A Comparison of Modeling and Monitoring Tools

Gary T. Hunt (Chairman)  
ERT  
696 Virginia Road  
Concord, MA 01742  
(617) 369-8910  
Dr. Larry Johnson (Co-Chairman)  
U.S. EPA  
Air and Energy Engineering Research Laboratory  
MD-62  
Research Triangle Park, NC 27711

**10. TCDD's, TCDF's and Other Air Toxics from Fire Situations**

Paul Shapiro (Chairman)  
Office of Research and Development (RD-681)  
U. S. EPA  
401 M St., SW  
Washington, DC 20460  
(202) 382-2583

**11. Risk Assessment and Management of Air Toxic Emissions from Chemical Facilities**

Chris Keyworth (Chairman)  
ERT  
696 Virginia Road  
Concord, MA 01742  
J. S. (Steve) Arendt (Co-Chairman)  
JBF Associates Inc.  
Technology Drive  
1000 Technology Park Center  
Knoxville, TN 37932

**WATER (8 Sessions)**

Dr. Steve C. Chiesa Area Coordinator  
Dept. of Civil Engineering  
Santa Clara University  
Santa Clara, CA 95053  
(408) 554-4097

**1. The Application of Chemical Engineering Fundamentals to Environmental Control**

Dr. William Ollinger (Chairman)  
Department of Chemical and Biochemical Engineering  
Rutgers University  
P.O. Box 909  
Piscataway, NJ 08854  
(201) 932-2228

**2. Pollutant Removal Techniques for Dilute Aqueous Streams**

Robert Kenson (Chairman)  
Metpro Corporation  
P.O. Box 144  
Harleysville, PA 19438  
(215) 723-6751  
Dr. P. K. Lim (Co-Chairman)  
School of Engineering  
NC State University  
P.O. Box 7905  
Raleigh, NC 27695-7905  
(919) 737-2328

**3. Groundwater Quality Protection—Evaluation of "State-of-the-Art" Technologies**

Dr. Peter Shanahan (Chairman)  
ERT, Inc.  
696 Virginia Road  
Concord, MA 01742  
(617) 369-8910

**4. Groundwater Contamination—Innovative Remedial Measures**

Dr. David Kosson (Chairman)  
Department of Chemical and Biochemical Engineering

Rutgers University  
P.O. Box 909  
Piscataway, NJ 08854  
(201) 932-2228

David Andrews (Co-Chairman)  
ERT, Inc.  
696 Virginia Road  
Concord, MA 01742  
(617) 369-2910

**5. Biotechnology and Pollution Control**

Dr. Steven C. Chiesa (Chairman)  
Department of Civil Engineering  
Santa Clara University  
Santa Clara, CA 95053  
(408) 554-4697  
Larry Southwick (Co-Chairman)  
ERT, Inc.  
Porter Building, 10th Floor  
601 Grant St.  
Pittsburgh, PA 15219  
(412) 261-2910

**6. Out of Well Treatment Technologies for Deep Well Injection**

Dr. Robert Irvine (Chairman)  
Department of Civil Engineering  
University of Notre Dame  
P.O. Box G  
Notre Dame, IN 46556  
(219) 239-6306

**7. In-Plant Modification for Waste Stream Reduction (Panel Discussion)**

Dr. Robert C. Ahlert (Chairman)  
Department of Chemical and Biochemical Engineering  
Rutgers University  
P.O. Box 909  
Piscataway, N.J. 08854  
(201) 932-2228  
Michael Overcash (Co-Chairman)  
Department of Chemical Engineering  
North Carolina State University  
Raleigh, NC 27695-7905  
(919) 737-2325

**8. Innovative Techniques for Pollution Control in the Chemical Industry**

Dr. Richard B. Kapuscinski (Chairman)  
Department of Civil Engineering  
University of Michigan  
108 Engineering I-A Building  
Ann Arbor, MI 48109  
(313) 763-9666  
Dr. Bruce Jones (Co-Chairman)  
Paper Products Div.  
Proctor and Gamble, Inc.  
6100 Center Hill Rd.  
Cincinnati, Ohio 45224  
(513) 659-4601

## SOLIDS (11 Sessions)

Dr. B. T. Delaney Area Coordinator  
Ground/Water Technology, Inc.  
100 Stickle Avenue  
Rockaway, NJ 07866  
(201) 625-5558

- 1. Fundamentals of Waste Incineration**  
William Tambo (Chairman)  
Environmental Research and Technology (ERT)  
696 Virginia Road  
Concord, MA 01742
- 2. Innovative Techniques for Hazardous Waste Control**  
Harry Freeman (Chairman)  
U.S. EPA  
Office of Research and Development  
Hazardous Waste Engineering Research Laboratory  
Cincinnati, OH 45268
- 3. Decontamination of Soils**  
Leo Weitzman (Chairman)  
Acurex Corporation  
P.O. Box 13109  
Research Triangle Park, NC 27709  
(919) 544-4535  
Dr. Michael Overcash (Co-Chairman)  
Dept. of Chemical Engineering  
Box 7905  
Raleigh, NC 27695-7905  
(919) 737-2325
- 4. Barriers to Implementing New Technologies for Treatment and Disposal of Hazardous Wastes**  
W. D. Byers (Chairman)  
CH2M Hill  
2300 N.W. Walnut Boulevard  
Corvallis, OR 97330
- 5. Fate and Transport of Constituents During Deep Well Injection of Hazardous Waste**  
Dr. Charles A. Wentz (Chairman)  
Waste Management Division  
Energy Research Center  
University of North Dakota  
Box 8213, University Station  
Grand Forks, ND 58202  
(701) 777-5235  
Dr. David Constant (Co-Chairman)  
Department of Petroleum Engineering  
LSU  
Baton Rouge, LA 70803-6417  
(504) 388-5215
- 6. Where Do We Stand on Superfund?**  
Dr. Edward Martin (Chairman)  
Peer Consultants, Inc.  
1160 Rockville Pike  
Suite 202  
Rockville, MD 20852
- 7. State Mandated Site Assessment Prior to Land Disposal**  
Edward A. Hogan, Esq. (Chairman)  
Lowenstein, Sandler, Brochin, Kohl, Fisher,  
Boylan and Meanor  
65 Livingston Avenue  
Roseland, NJ 07068

- 8. New LUST Regulations**  
Daniel Moon (Chairman)  
GCA Technology Division  
213 Burlington Road  
Bedford, MA 01730
- 9. University Graduate Research in Environmental Control Fundamentals**  
Dr. Robert C. Ahlert (Chairman)  
Rutgers University  
Dept. of Chemical and Biochemical Engineering  
Busch Campus  
P.O. Box 909  
Piscataway, NJ 08854
- 10. Closing Hazardous Waste Lagoons-State-of-the-Art**  
Peter S. Daley (Chairman)  
Director of R and D  
Chemical Waste Management, Inc.  
150 W 137 St.  
Riverdale, Ill. 60627
- 11. Practices and Effects of Offshore Drilling Wastes**  
Dr. Charles A. Wentz (Chairman)  
Waste Management Division  
Energy Research Center  
University of North Dakota  
Box 8213, University Station  
Grand Forks, ND 58202  
(701) 777-5235  
Mr. James E. Leeman (Co-Chairman)  
Surface Water Program  
Conoco Inc.  
Marland Building, Room 1138  
600 North Dairy Ashford Rd.  
Houston, Texas 77079  
(713) 293-3609

## NEW! Pump Literature



from laboratory to pilot plant, to full production...American LEWA offers a sealless, **leakfree** solution:

### Triplex Diaphragm Pumps:

For production processes to 5,000 psi and 50,000 gph. Zero-leakage, low-maintenance design. Ask for Catalog D1-005.

### Diaphragm Metering Pumps:

For services up to 17,000 psi and 18,000 gph. Modular design for versatile applications. Ask for Catalog D2-200.

### Laboratory Pumps:

To meter to 710 psi and 1,800 ml/hr, hermetically sealed and non-contaminating design. Ask for Catalog D1-251.

For hazardous or harmless fluids, American LEWA pumps pay for themselves in reliable, low-maintenance and safe operation. Call 617-429-7403 or write today!

**AMERICAN LEWA®**

132 Hopping Brook Road  
Holliston, MA 01746

# Recommendations for the Regulation of Air Toxics

To assist federal, state, and local government officials concerned with the protection of our nation's air quality from pollutants, this paper was prepared by the Air Quality Task Force of the Government Programs Steering Committee of the American Institute of Chemical Engineers (AIChE).

**Jacoby A. Scher**  
Principal Author

## I. Introduction

The Government Programs Steering Committee (GPSC) of the American Institute of Chemical Engineers (AIChE) has long been concerned with reasonable and technically sound solutions to our Nation's environmental problems. As chemical engineers we believe that the employment of proven scientific and engineering principles, as well as innovative approaches to the solution of these problems, must be considered in the promulgation of legislation and subsequent regulations.

Such legislation and regulation designed to remove harmful substances from the environment are necessary and desirable, but our laws must address these issues in a realistic and workable manner. Prior legislation, such as Section 112 of the Clean Air Act, introduced a perspective that would essentially provide a "zero risk" climate. While this may be an ideal goal, legislators must acknowledge that "zero risk" is unattainable—impossible to achieve because of the basic laws of science, as well as the economic realities and constraints involved.

GPSC believes that if the following technical program elements are included in the regulations, they could provide a more effective mechanism for the regulation of toxic air pollutants and could possibly be a model for other environmental regulation.

*Note: This commentary addresses only the chronic effects of chemicals relative to their impact upon the environment and the population at risk.*

## II. Technical Components for Consideration

The major technical components to be considered for inclusion in legislation which addresses the regulation of air toxics are:

### A. Reassessment of Section 112—Clean Air Act

As previously stated, the use of the phrase "ample margin of safety" has been construed to define a zero risk scenario. However, there is no definitive method to set this margin and no uniform level upon which such a margin can be established. With the inclusion of that phrase as an unquantifiable entity, the use of risk assessment becomes meaningless. We believe that the phrase "ample margin of safety" should be eliminated or modified in Section 112 and the following elements should be considered.

1. A more intensive focus on those pollutants which have the greatest potential as health hazards.
2. The creation of rigorous scientific procedures, including peer review, in order to develop the necessary background data that will encompass the health effects of individual pollutants.
3. Modification of the "ample margin of safety" clause to include words that encompass procedures committed to reasonable risk assessment.
4. Consideration of the effects of standard setting on our industrial network and economic climate as well as on the public health and welfare.

### B. Consideration of Reasonable Time Frames for Evaluation & Regulation

Chemical emissions of toxic and hazardous air pollutants have been present throughout history. For example, wood burning fires are known emitters of hazardous air pollutants. There are many natural chemicals which provide a considerable risk to both public health and the environment. The industrial revolution only exacerbated the problem of chemical air emissions, but the problem is neither unique nor new. More recent incidents have focused interest upon rapid and strict enforcement of emission controls; however, to mandate controls without a valid scientific basis for such controls is inappropriate and possibly counterproductive.

*GPSC believes that Congress, when enacting regulatory legislation, should set an appropriate time frame for regulatory administration of toxic air emissions based upon valid, scientifically defensible data and a reasonable assessment of the risk to the public health and environment. The proper institutions necessary to address the pertinent issues and develop the scientific information, should be established (while not overlooking the necessity to proceed expeditiously). There exists a great body of underutilized scientific and engineering talent which, if properly administered, could devote its efforts to enhance the initiation and maintenance of the program as outlined.*

### **C. Use of Emission Standards rather than Ambient Standards for Control**

GPSC believes that the intent of the Clean Air Act, to control hazardous air pollutants at the emission source, is technically correct and it is only at that point that measurements are accurate and technological control is achievable. However, instead of uniform national standards, site specific emission standards employing controls which achieve some minimum reasonably achievable emission levels are recommended. Additionally, the site specificity should account for the population at risk as determined by risk assessment and dispersion modeling.

### **D. Use of Approved Consensus Dispersion Models to Relate Emissions to Chronic Exposure Values**

Obviously the basis for any characterization of a chemical as carcinogenic, hazardous, etc. will be dependent upon that chemical's effect upon the human or other biological species. While the prediction of the degree of carcinogenicity or hazard of a chemical is a problem unto itself, it must be relatable back to the source of the emission. Air dispersion modeling has progressed significantly in the last decade and it is now possible to use dispersion models to relate the assigned chronic exposure values back to the controllable emission source. It should be noted that models are only technically adequate for *chronic* effects and are not reliable for *acute* impacts. They are also *not* as reliable for heavier than air components as for lighter than air components. As an initial basis for regulating particular chemicals, recognized exposure values as promulgated under OSHA, MSHA, the National Cancer Institute and other recognized institutions can be used. *To develop a complete analysis of the impact of new facilities upon the population at risk, new risk assessment models must be developed.*

### **E. Use of Existing State Permit Programs for Administration**

*Efficient permit mechanisms already exist at the State level to administer such a program.* There seems to be little need to superimpose another burdensome permit program upon one that has been proven to be effective and accepted. The State permit programs provides reasonable intimate contact between the regulator and the emitter, and such an interface is necessary for implementation of the program.

### **F. Use of Risk Assessment for Determining Regulated Species and the Acceptable Level of Risk**

The GPSC as well as many scientific and engineering institutions have recommended that risk assessment be a necessary component of all environmental regulation. It is an accepted tool in the scientific community and for years has been utilized within the Federal Government, particularly the Department of Defense. While not without flaws, risk assessment, properly implemented, provides a strong technical basis for the regulation of individual chemical species. *GPSC strongly recommends that risk assessment, in conjunction with other elements of this proposal, be at the core of any air toxics legislation.* This is best achieved by using air dispersion models to determine emission levels that could be allowed, without exceeding desired ambient air quality levels with known risk profiles to the public. It is also important to recognize that risk assessment and risk management should be *separated* within the regulatory framework. In this context, risk management will be based upon political and socio-economic as well as technical considerations.

### **G. The Protection of Industrial Proprietary Information**

There has been considerable impetus in the last few years to provide information on the environmental effects of chemicals to the American public under Community Right-to-Know legislation. *While such information is necessary to formulate emergency response programs, it is also absolutely necessary for industrial trade secret and process information to remain proprietary.* The recent Dow Chemical case in Michigan is an example of intrusion upon process propriety which must be protected. Technological advances are made in the spirit of free enterprise and competition, and without such protection, the viability of future advances in American science and engineering become questionable. GPSC recommends that propriety processes be protected and that Materials Safety Data Sheets be used for informing the public of chemical hazards.

### **H. Regulation of Chemicals**

*GPSC recommends that only those chemicals or families of chemicals which are quantifiable analytically and have been scientifically proven to be hazardous, be addressed under the regulatory umbrella of future legislation.* The criteria should be flexible and reviewable by a Peer Group, depending upon the development of new chemicals and/or new scientific evidence concerning the chemicals under review. This component is obviously the crux of the matter, because at this point we move from concept to real numbers and questions concerning measurable detection limits of chemicals; scientifically defensible levels of risk of chemicals; and the engineering ability to control such emissions. Unless Congress is willing to address such issues, there will be no quantification of the risk. It is also equally important to *not* regulate to the analytical detection measurement per se, unless there is a scientific determination that such chemicals at these levels provide an inordinate amount of risk to the public health and the environment.

### **I. Peer Review System**

*GPSC recommends that a scientific peer review system be established as an integral part of any legislation which deals with scientific methodologies and risk assessment.* This entity must be as independent as possible and certainly above reproach. It must have clear direction and possible extraordinary powers because in a sense, it will be the key protector and decider of what levels of risk are acceptable and how much protection the American public and our environment will have.

### **III. Summary**

The Government Programs Steering Committee of AIChE recognizes that the control of hazardous air pollutant emissions is necessary for the protection of the public health and environment. Contained within this paper are recommendations for the major elements of any such proposed legislation.

GPSC feels that inclusion of these major components in any proposed air toxics legislation will provide protection of the population at risk without unduly burdening our present industrial and regulatory systems.

GPSC further believes that there are other questions and issues to be addressed in formulating a technically based and economically reasonable air toxics legislative program.

1. Is a multitiered hazard classification of chemicals desirable or necessary ala the Food and Drug Administration?
2. What are acceptable risk levels vis-a-vis some measurable standard, i.e., mortality, incidence of cancer, crop reduction, termination of industries, etc.?
3. Should motor vehicles be regulated?
4. Should both new and old sources be regulated?
5. How do we reach "consensus" on acceptable levels of risk and who casts the votes?
6. Should we promulgate uniform standards or State/Regional standards or a combination of both?

These issues will be addressed in future GPSC commentaries. Select GPSC members are available for further discussion and or testimony.

---

*For additional information contact: Dr. Martin Siegel, Staff Director—Government Relations, American Institute of Chemical Engineers, 1707 L Street, NW St. 333, Washington, DC 20036. Telephone: (202) 223-0650.*



The following three papers were originally scheduled to appear in our special "Heavy Metals Separations" issue published in May 1987 and edited by Robert W. Peters. The papers appear here because of lack of space in the May 1987 issue.

# Membrane Utilization in Hazardous Metal Removal from Wastewater in the Electronic Industry

S. Sternberg

Memtek Corporation, Billerica, MA

*Membrane treatment of industrial wastewaters is limited to a few applications where the membrane properties and environmental resistance match the particular application. In most cases, however, the membrane in and by itself does not possess all the requirements for the application, such as chemical and physical resistance and inherent capability to remove all the waste components.*

*The process described here overcomes these limitations by creating an inert membrane whose task is dewatering only, and relying on chemical and physical pretreatment to render the soluble waste constituents insoluble particles which are then removed by the membrane.*

## INTRODUCTION

A semipermeable membrane is a thin, soft, pliable sheet or layer through which certain species can pass while others cannot or their passage is retarded. This ability to distinguish between and separate species is the most useful property of the membrane. The species may be distinguished according to their thermodynamic characteristics (solubility in the membrane matrix), kinetic characteristics (Diffusion in the membrane matrix) their charge, or simply their physical size, as in (fluid) filtration. This discussion will be limited to polymeric membranes, i.e., the membrane matrix is made of a polymer or polymer blend or mixture. The membrane may or may not be porous.

It is obvious that the smaller the species to be rejected by the membrane, the smaller the "pore size" or the passageway through the membrane should be. When the species to be removed is a soluble ion, the passageway becomes a diffusion-permeation path rather than a pore. As the size of the removed species increases, so can the size of the pores and actual flow through pores in the membrane become the main mode of transport.

Permeability (or Solution-Diffusion) transport is a relatively slow process. Transport occurs on a molecular scale, where molecule by molecule the permeating species moves across the membrane under a pressure and/or concentration gradient. This is usually the operating process when small molecules have to be separated: e.g. gas separation, Reverse Osmosis. This mechanism requires high pressures to affect acceptable fluxes for commercial applications.

Ultrafiltration ranks next with regards to size of species being removed. The membrane is still capable of removing soluble species such as proteins and other high polymers, but is completely permeable to small ions. Op-

erating pressures in Ultrafiltration Applications are usually an order of magnitude lower than those in Reverse Osmosis, with similar or slightly higher fluxes.

Larger pore sizes are found in Microfiltration Membranes. Here no soluble species is removed, and the filtration is strictly physical exclusion by size. Particles larger than the membrane pore size will be retained or rejected by the membrane. Obviously, any soluble species will pass freely. Applications pressures are very low and fluxes are orders of magnitude higher than those of Reverse Osmosis or Ultrafiltration (See Table 1).

The applications pressures and fluxes described above refer to the inherent capabilities (The "Inherent Capability" of a membrane is its flux when pure water with no rejected species is passed through it) of the membranes themselves, without regards to the so called "Concentration Polarization" or cake formation. These phenomena always occur once a species is rejected by the membrane. As the non-rejected species or fluid is passing through the

TABLE 1. PHYSICAL PARAMETERS OF MEMBRANE PRODUCTS

	Reverse Osmosis	Ultra-Filtration	Advanced Membrane Filtration
Pore size, Microns	0.001	0.01	>0.1
Operating Pressure kPa (psi)	2,800->7,000	350-700	280-350
Flux Rate l/mh (gfd)*	400->1,000	(50-100)	(40-50)
	17-43	50-130	340-680
	(10-25)	(30-75)	(200-400)

\* l/mh = L/m<sup>2</sup> of Membrane/Hour  
gfd = gal/ft<sup>2</sup> Membrane/Day

membrane, the rejected species accumulates at the membrane interface and forms a layer containing a high concentration of this rejected species. In most applications it is the resistance to flow of this layer that is controlling the flux rate of the system, and not the membrane itself. It is not surprising therefore, that fluid flow management is so important in membrane applications, since reduction of the resistance of this layer results in higher fluxes thus higher efficiencies and lower costs. (see Figures 1 & 2)

## BACKGROUND

From the foregoing paragraphs it seems apparent that reverse osmosis alone is the mechanism to be used in most waste treatment applications, since small soluble molecules and ions are to be removed in most of these applications. This would be true if all factors other than removal or rejection were to be neglected. However, factors which are ultimately economical must be considered, and these in most cases dictate the choice of the process.

Current reverse osmosis membranes suffer from insufficient chemical resistance when applied to most waste treatment applications: pH environments and/or oxidizing agents destroy the rejection capabilities of these membranes, so that their utilization is limited to cases where the waste is well controlled relative to these factors, to stay within the boundaries tolerated by these membranes. The high pressure requirements, coupled with relatively low fluxes and recovery also make this approach uneconomical in most cases.

The ideal membrane should exhibit high fluxes at low pressure, high rejection of unwanted species, high recovery (i.e. ability to maintain high concentration of rejected species without deterioration of flux), and high resistance to chemical and biological attack. All these properties must be maintained for long periods of time to allow for uninterrupted process.

A new innovative approach to utilization of membranes in waste treatment is presented in the following paragraphs. This approach involves the manipulation of the wastewater prior to introducing it to the membrane, making the waste stream compatible with the membrane of choice. The membrane of choice is a high flux asymmetric membrane which by itself will not reject any soluble species. The membrane is made of an inert polymer which can tolerate the entire pH range and any oxidizing environment. To facilitate appropriate fluid flow management, the membrane is cast on the inside of a one inch diameter porous support tube, to allow high velocity, turbulent flow along the membrane surface, thus minimizing concentration polarization and/or cake formation.

Qualitative inspection of Figures 3 and 4 reveals that for economical high flux low pressure applications one must use relatively large pore size membranes. However, these membranes are not expected to reject soluble species. In the present approach, instead of modifying the membrane to remove the soluble species, the waste water is treated in such a way as to convert the soluble species to insoluble, relatively large particles which *are* removed by the membrane of choice. Thus instead of manipulating the membrane to fit the wastewater, the wastewater is treated to fit the membrane.

"Pretreatment" includes chemical and/or physical alteration of the soluble species: e.g. pH adjustment, oxidation-reduction, adsorption-absorption schemes, etc. The common denominator to all pretreatment is the conversion of the soluble species to large, insoluble particles. Chemical pretreatment may be as simple as raising the pH of the metal bearing solution, to form and precipitate metal hydroxide particles. Other insoluble metal salts include sulfides [1, 2], diethyldithiocarbamate (DTC) salts [3, 4], and others more specific to the particular metal. Also, reduction of the soluble metal ion to its metallic form will create filterable particles — reducing agents such as sodium borohydride [5], sodium hydro-sulfite, sodium meta bisulfite and others have been used. An interesting approach, first proposed by Shorr [6] is coprecipitation of metal cations with excess ferrous hydroxide. It seems that the precipitating ferrous hydroxide particles incorporate within their matrix other metal ions scavenged from the solution. This approach allows removal of soluble metals to limits which are orders of mag-

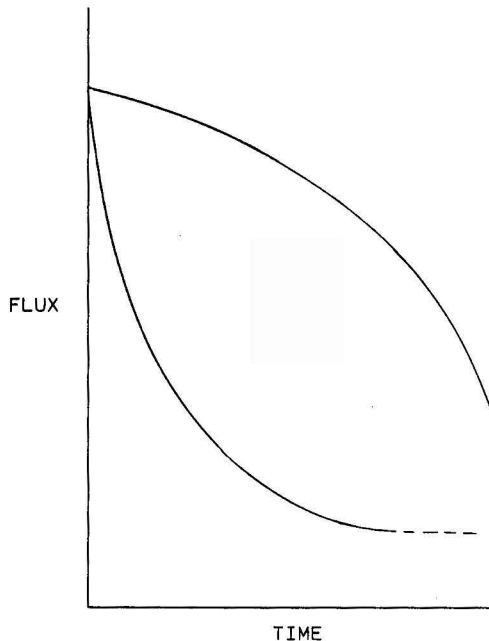


Figure 1. Flux decay with time.

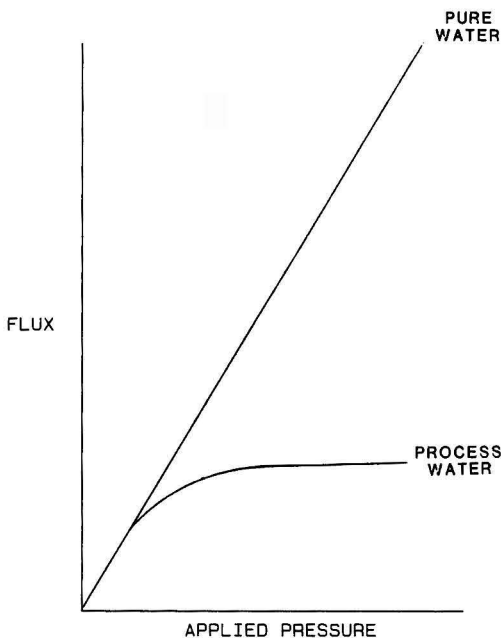


Figure 2. Membrane flux vs. applied pressure.

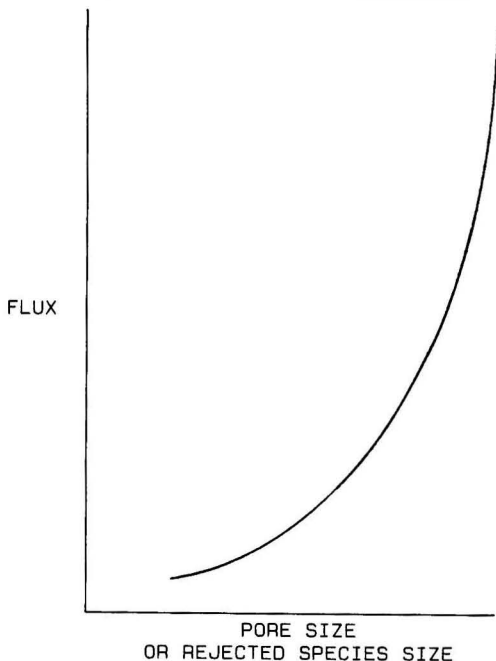


Figure 3. Typical membrane flux vs. species size.

nitude lower than their thermodynamic solubility limit. In general it can be stated that coprecipitation of several metal ions usually results in lower residual soluble metal concentrations than those predicted from thermodynamic solubility parameters.

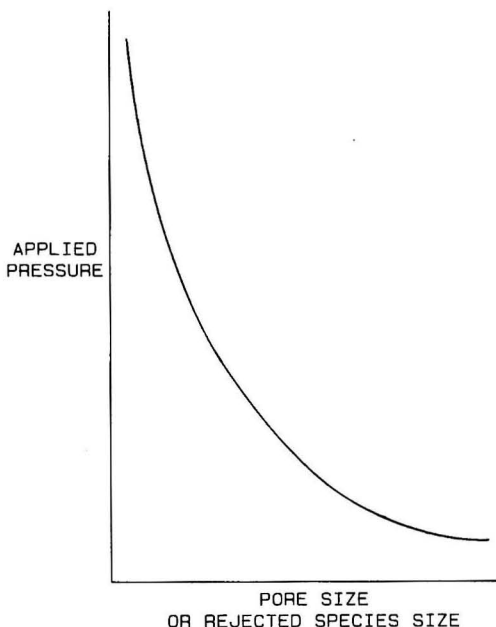


Figure 4. Pressure required vs. rejected species size.

Particulate adsorbent such as carbon black, bentonite, diatomaceous earth, glass beads and other activated or inert ones have been used successfully to remove soluble metal ions from solutions. Combination of adsorbents and chemical manipulation often results in synergism, presumably due to easier access of the reacting species to the adsorbed one.

The membrane of choice is an asymmetric membrane, where the pore opening on the side exposed to the incoming treated wastewater is much smaller than the size of the rest of the pore. The model for such membrane is depicted in Figure 5. In the current membrane the pore opening is on the order of  $0.1 \mu\text{m}$ , thus all particles larger than that will be rejected. Only occasionally can a particle this small be formed, most particles created by the pretreatment procedures are much larger, thus are rejected. The asymmetry of the membrane is crucial to maintenance of high fluxes: examination of Figure 5 shows that if an occasional particle of the same size as the pore opening or smaller is encountered, it will go through without hindering further flow. Had the pore structure and size been even throughout its length, such particle would be likely to get lodged against the walls along the pore and block it. Larger particles will be swept away along the membrane face by the high velocity flow, and will not accumulate to form a barrier to flowthrough.

Fluid flow management is achieved by high pumping rates of the wastewater through the tubular membranes. The fluid linear velocities are 12-15 Ft/Sec, resulting in Reynolds numbers in excess of 100,000. The boundary layer under these flow conditions is exceedingly thin, thus concentration polarization and cake formation are minimized.

The system is comprised of a pretreatment compartment including all the reaction tanks, sensors and metering pumps to jointly perform the conversion of the soluble species to insoluble particles. The treated fluid is then pumped from this compartment to the membrane compartment where the insoluble particles are concentrated in the membrane circulation loop and the purified water permeating radially through the membrane and porous support tube is collected either for disposal or reuse. Further thickening and dewatering of the sludge circulating in the membrane loop is achieved by bleeding the sludge into a thickener and/or filter press. Figure 6 is a schematic presentation of the system, with an idealized mass balance assuming 0.01% (100 mg/l) influent concentration and zero concentration in the permeate; additive chemicals were neglected.

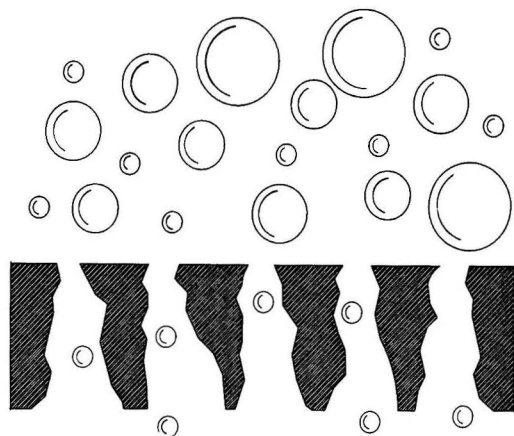


Figure 5. Partial rejection by asymmetric membrane.

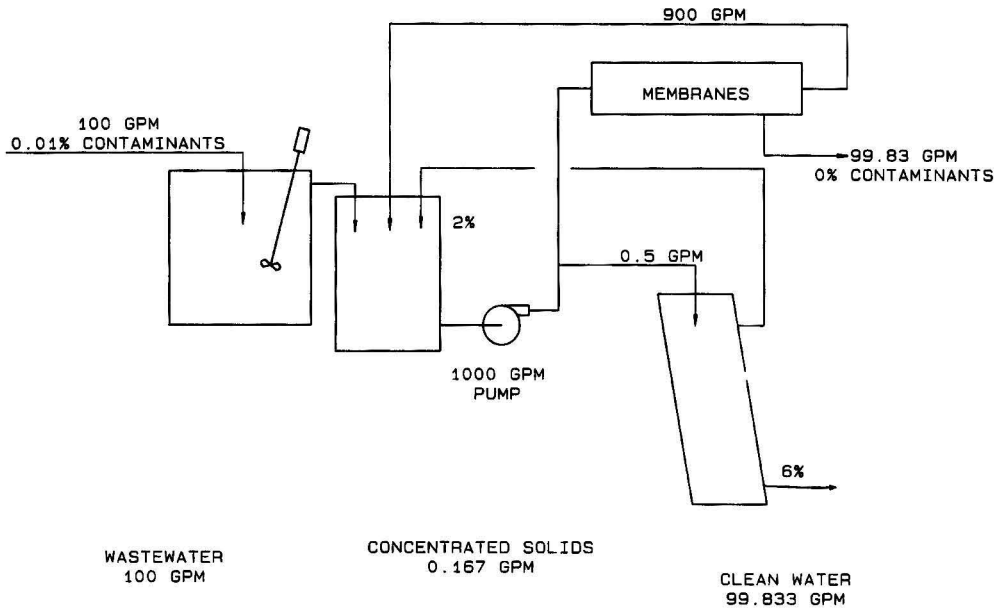


Figure 6. The Memtek System.

**APPLICATIONS**

The following are descriptions of and results from some operating plants utilizing the subject approach:

tem provided by Memtek. All other metals are non-chelated. The wastes are combined in a single reaction tank and pH is adjusted with NaOH. Concentrates (including alkaline cleaners) are transferred to a concentrate tank and metered into the feed water.

The Waste Characteristics are as follows:

**Plant A**

**A Plater of Electronic Components and Connectors**

Waste is from general metal finishing. Total flow is 56 gpm. There is 3-10 gpm of cyanide which is segregated and processed through a two-stage cyanide destruct sys-

	Feed	Filtrate	Limits	Memtek Guarantee
Cu	1.0	0.03	3.5	1.09
Ni	31.6	0.6	4.0	1.26
Pb	4.2	.1	0.7	.23
CN <sup>-</sup>	5.0	.02	1.2	.28
Zn	1.5	.1		

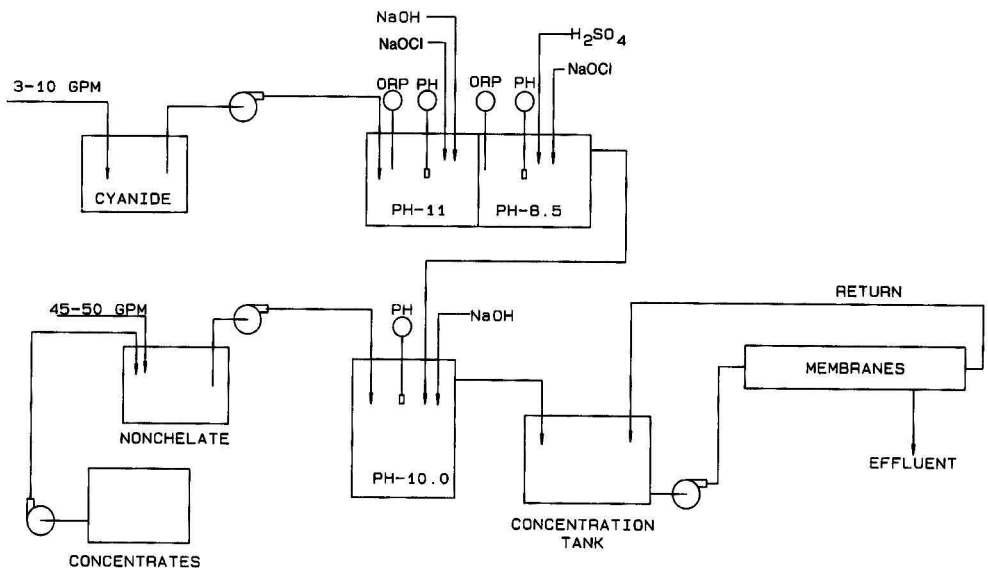


Figure 7. Plant A.

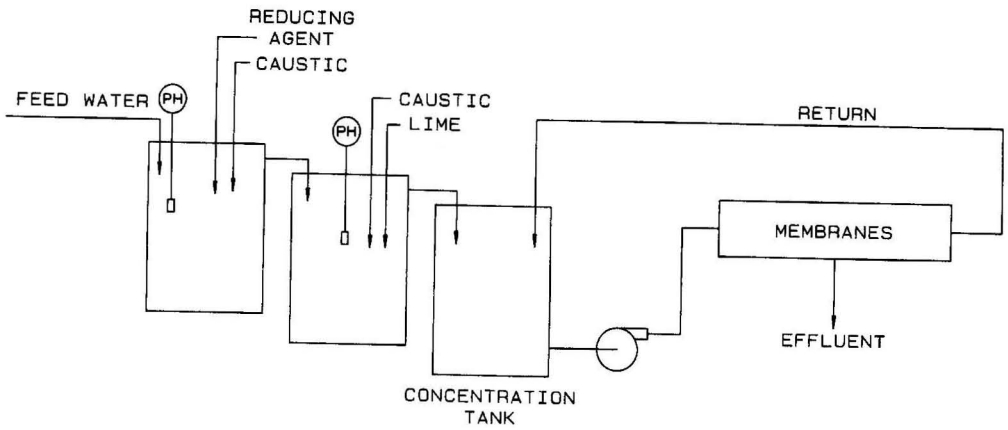


Figure 8. Plant B.

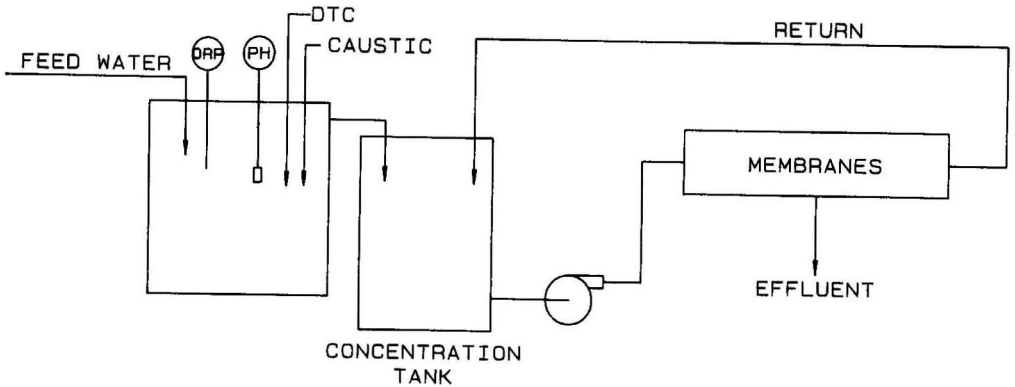


Figure 9. Plant C.

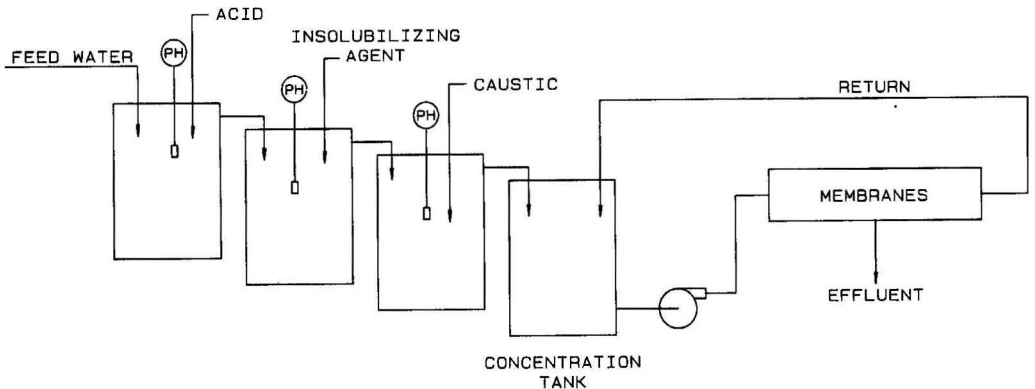


Figure 10. Plant D.

**Plant B**

Wastewater from wave soldering operation contains relatively high concentrations of lead which must be removed. In this specific plant, the influent is 20 gpm of wastewater, at pH < 1.0, containing 25-50 mg/l of lead, to be reduced to less than 0.4 mg/l in the effluent. A portion of the soluble lead in the influent is chelated, thus simple

pH adjustment will not be effective.

The Memtek system operating successfully in this application is described in Figure 8. The reducing agent of choice here is ferrous sulfate which is converted to ferrous and ferric hydroxide. As described before, the ferrous ion here is used both as a reducing agent and a coprecipitant. Treatment cost including power, chemicals and sludge handling is in the \$2-3/1000 gallons range.

### Plant C

This is a typical Printed Circuit Board plant, the wastewater of which contains copper, nickel and lead at concentrations of about 65, 10 and 5 mg/l, respectively.

The wastewater treatment plant supplied by Memtek is described in Figure 9. This is a 35 gpm turnkey plant which includes a concentrate bleed system and a filter press dewatering system in addition to the main wastewater treatment system. The plant has been in operation for over two and half years now, producing consistently effluent containing 0.1 mg/l copper, 0.1 mg/l nickel and 0.3 mg/l lead.

The treatment process utilizes diethyldithiocarbamate (DTC), which is useful in treating chelated species present in the wastewater. The addition of DTC is controlled by ORP to optimize reaction and minimize chemicals cost and production of sludge. The cost of this treatment is in the range of \$4-5/1000 gallons, including power, chemicals and sludge handling.

### Plant D

Gallium Arsenide chip manufacturing produces wastewater containing Ga, As and  $F^-$  which must be removed. Memtek has developed a process which removes arsenic to less than 100 ppb in the effluent.

The system is designed to process both wastewater and concentrates from the operations. Treatment cost is in the range of \$3-4/1000 gallons, including power, chemicals and sludge handling. The three-step operation is described in Figure 10.

### LITERATURE CITED

1. Scott, M. C., EPA-600/8-79-014, 1979.
2. Yeliger, M. B., G. Bagenski, and R. M. Schlauch, EPA-600/52-81-142, 1981.
3. Wing, R. E. and W. E. Rayford, *Plating & Surface Finishing*, 69(1), 67-71 (1982).
4. Pollution Technology Systems Inc., Tech. Data Sheet PTS 483-DX-2000.
5. Lindsay, M. J. and M. E. Hackman, Purdue Research Foundation, 1985.
6. Shorr, J., U.S. Patent #4,014,787, 1977.



**Shmuel Sternberg** is Vice President of Research and Development for Memtek Corporation, and is responsible for the firm's membrane and products development. Prior to joining Memtek, he held Senior Technical positions with Millipore, Abcor and Amicon Corporations. He earned a B.Ch.E. from Georgia Tech, M.Sc. from Carnegie Tech and a Ph.D. from Case Western Reserve University.

# Removal of Heavy Metals in Wastewater in a Clay Soil Matrix Using Electro-Osmosis

Chittaranjan Ray and R. H. Ramsey

Department of Civil Engineering, Texas Tech University, Lubbock, TX 79409

*The feasibility of using electro-osmosis for removal of heavy metals (Cd, Cu, and Pb) contained in aqueous solutions was examined using soil cores formed from Randall clay — a clay found in Playa lake basins in the High Plains of West Texas. Initially, sorption tests were conducted with the clay dispersed in the metal solutions of interest to determine if adequate sorption would take place. The retention capacity of the clay for Cd was found to be 0.0083 mg/mg of soil. ( $10^5$  kilograms of Cd could be removed in top one-meter depth of a hectare of Randall clay with a bulk density of  $1.4 \text{ g/cm}^3$ ).*

*Electro-osmosis was found to increase the permeability of the clay but was found to be both a slow rate system (up to 225 days to remove one pore volume of water through a  $\text{m}^3$  of soil) and energy intensive ( $1.44 \times 10^5 \text{ kJ}$  to  $8.1 \times 10^5 \text{ kJ}$  per  $\text{m}^3$  of drained water). Problems noted during the test that need solution before further experimentation with this procedure include selection of less corrodible materials for electrodes, prevention of electrolysis of water at potential gradients needed to move the waters being treated through the soil matrix, and control of ion gradients from the anode to the cathode reservoir to prevent backflow episodes from reversing flow from the cathode to the anode region.*

## INTRODUCTION

Electro-osmosis is a physico-chemical phenomenon which involves the application of a direct current (DC) potential across a fine porous capillary system containing colloidal particles (such as a clay soil matrix) to improve its permeability. Water movement in a capillary system through the influence of electro-osmosis has been demonstrated under both laboratory and field conditions. Under the application of electro-osmosis, water particles, in general, move from the anode side of a clay soil core to the cathode side. If a positive hydraulic gradient exists from the anode side of the imposed potential to the cathode side, electro-osmosis is normally observed to increase the soil solution flow.

The theoretical basis of electro-osmosis is presented in standard soil physics texts and journals [1, 2, 3]. A moist or saturated clay soil can be considered to be a colloidal system in which a solid phase, i.e. clay particles, is dispersed in a liquid medium, i.e. soil water. The individual clay particle is surrounded by a thin layer of solution with electrical properties that differ from those of the bulk solution in the soil pores. This layer has a higher concentration of ions (either positive or negative) than the bulk solution. Each colloidal particle is surrounded by its shell of hydration, called a "micelle", which is firmly attached to the particle. When a particle is induced to move under

the application of an electric potential, the micellar fluid also moves thus causing a flow of liquid. In this process, the viscosity of the soil water resists the movement of the moisture film; thus, the mobile part of the film must overcome the shearing resistance of the liquid.

The velocity of electro-osmotic fluid flow across a capillary system (or a clay soil matrix) is directly proportional to the applied voltage gradient and the specific surface area of the particles and is inversely proportional to the viscosity of the fluid. The electro-osmotic flow rate in a single capillary under a potential difference of  $E$ , as derived by Casagrande [4] from the improved Helmholtz equation of electric double layer, has the following form:

$$Q_e = \frac{\zeta DEr^2}{4Z\eta} \quad (1)$$

where  $Q_e$  = volume of liquid moved per unit time, mL/min  
 $\zeta$  = zeta potential, volts  
 $D$  = dielectric constant of the fluid  
 $Z$  = length of the capillary tube, cm  
 $\eta$  = coefficient of viscosity of the fluid,  $\text{mPa} \cdot \text{s}$   
 $E$  = potential difference across length  $Z$ , volts, and  
 $r$  = radius of the capillary tube, cm

If one considers a cylindrical soil core of length  $Z$  and cross-sectional area  $A$  in contact with the electrodes, equation (1) may be rewritten as:

Chittaranjan Ray is presently with Ceraghty and Miller, Inc., 7 Atlantic Street, Hackensack, New Jersey 07601.

$$Q_e = \frac{\zeta Dq}{4\eta} \cdot \frac{E}{Z} \cdot A \quad (2)$$

where  $q$  is an empirical factor related to the porosity of the core and to the cross-sectional area of the pore space through which the fluid moves. Further, equation (2) may be written in the form of the Darcy equation:

$$Q_e = k_e \cdot i_e \cdot A \quad (3)$$

where  $k_e = \frac{\zeta Dq}{4\eta}$  is the electro-osmotic permeability and

$i_e = \frac{E}{Z}$  is the potential gradient. Although equation (3)

describes the theoretical rate of fluid flow in a soil core under a given potential gradient, the principal uncertainty is associated with the value of  $q$ . Furthermore, this equation does not take into account the effect of interfering factors such as the possible compression of the double layer because of high salinity, loss of electrical energy through the electrolysis of water, and the reactions of the electrode material with the chemicals in water.

The concept of electro-osmosis was first applied to field situations involving the dewatering of excavations by Casagrande in the 1930's [5]. The technique was later applied to electro-chemical hardening of clay to modify soil properties for pile driving operations [6].

More recently, this technique has been applied to solving wastewater disposal problems on soils of low permeability [7, 8]. In this method, wastewater is applied in adsorption trenches installed between an anode system that is constructed using crystalline rocks and a cathode system consisting of coke or graphite. This system is capable of developing a potential of 0.7 to 1.3 volts with sufficient current for electro-osmosis. A test conducted in California [7] showed an improvement in permeability from  $1.8 \times 10^{-4}$  to  $3.25 \times 10^{-3}$  cm/s. In another case, this system gave satisfactory results in disposing of septic tank effluents on heavy clay soils in North Dakota and Minnesota [8]. Generally, these soils, because of their low permeability, are not suitable for waste disposal through septic tanks and tile fields. It should be noted that the above system did not require external energy for operation. The authors designated this process as "sewage osmosis".

Normally, the objective of land treatment of municipal wastewater is to accomplish the removal of organic parameters from the wastewater. Advanced waste treatment techniques, other than land treatment, are required if dissolved inorganic parameters including heavy metals must be removed. These processes are energy intensive and costly. One approach to removing heavy metals from wastewater is to use land application systems located on soils with high sorption and cation exchange capacities. Soils with high clay content could serve this purpose. System design problems confronting engineers would then consist of locating large areas of naturally occurring clay soils needed for disposal of wastewater due to the low infiltration rates. To correct this situation, electro-osmosis obtained by imposing a direct current on a field installation of electrodes could be used. This process could increase hydraulic flow rates through the clay soils thus promoting higher rates of heavy metal removal while decreasing the land area required for wastewater treatment.

Alternatively, a treatment system could be constructed using a reactor filled with a clay. After saturating the clay, wastewaters containing the heavy metals could be applied to the system and electro-osmosis could be used to cause the wastewaters to flow through the clay matrix. After satisfying the sorption capacity of the clay, the spent material could be placed in a protected landfill or sent to a recovery unit for reclaiming the heavy metals.

To determine the applicability of electro-osmosis for increasing the flow of pollutant-laden water through a soil

with a high cation exchange capacity, a series of tests using samples of Randall clay was planned. This clay is locally available in the Playa lake basins of West Texas.

An electrolytic cell procedure of electro-osmosis, rather than the galvanic cell principle [7, 8] was considered for the tests. Smith [9] had suggested that the concept of "sewage osmosis" described by a licensee in the Midwest lacks theoretical backing. For these reasons electro-osmosis created by the use of an electrolytic cell was employed in this study.

## EXPERIMENTAL INVESTIGATION

The experimental investigation was designed to accomplish the following objectives:

1. determination of the sorption capacity of Randall clay for heavy metals;
2. determination of rates of soil solution flow under electro-osmosis;
3. identification of feasible electrode configurations that can be used in a low technology field system based upon the results of the bench-scale study; and
4. evaluation of the design and operation of full-scale systems based upon laboratory results.

### Adsorption Studies

A series of batch-type adsorption isotherm tests was conducted using samples of Randall clay to determine the sorption capacity for such heavy metals as Cd, Cu and Pb. Soils passed through a US No. 100 mesh screen sieve (0.147 mm) were used in this study. The solution was prepared with Cd, Cu and Pb in concentrations of 20, 20 and 50 mg/L respectively; the volume of solution prepared in each batch was limited to 40 mL. A neutral pH was maintained in the solution after the addition of soil. The masses of sorbents (soil) added to each solution were varied from 50 to 1000 mg. Periodically, the samples were mechanically agitated for about 10 days. Freundlich-type adsorption isotherms were plotted to describe the sorption characteristics of these heavy metals. The adsorption isotherm constants for the three metals are summarized in Table 1. Similar slopes and intercepts were observed for Cd and Cu, whereas Pb had a higher intercept value but a gentler slope indicating low sorption capacity at higher equilibrium concentrations.

Another series of adsorption tests was conducted for Cd using soil samples collected from different locations within a Playa lake basin in Lubbock County, Texas. Based upon visual observation, these soils contained varying quantities of clay and organic matter. A 75-g mass of soil was stirred continuously in 750 mL of a known concentration of Cd at constant temperature. Liquid samples were then withdrawn at 12, 24, 48, 72, and 120 hours and analyzed for Cd. A series of tests having been conducted at the beginning of the test runs to determine the optimum range of Cd concentrations and soil masses for this study, the test was conducted using high concentrations of Cd (1000 mg/L). From Figure 1, it was estimated that the maximum retention of Cd was 0.0083 mg/mg of soil. Theoretically, a similar soil with a bulk density of 1.4 g/cm<sup>3</sup> would be able to retain over 10<sup>3</sup> kilograms of Cd per

TABLE 1. FREUNDLICH ADSORPTION ISOTHERM CONSTANTS FOR SELECTED HEAVY METALS FOR RANDALL CLAY

Metal	k	n
Cd	0.0013	2.33
Cu	0.0010	2.51
Pb	0.0024	4.55



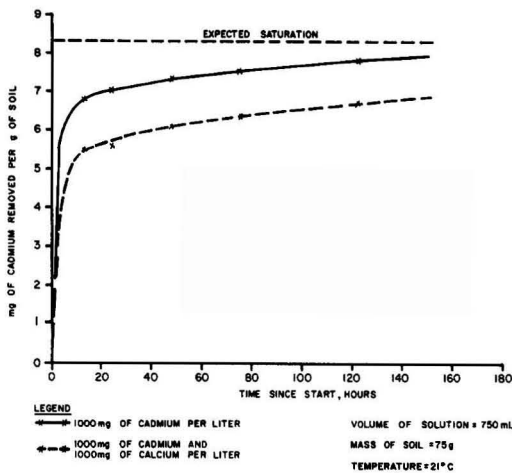


Figure 1. Sorption characteristics of Randall clay for cadmium.

hectare in the top one-meter depth. Thus, a total of 1000 m<sup>3</sup> of wastewater containing 10 mg/L of Cd could be applied per m<sup>2</sup> of soil before it would become saturated with Cd. Similarly, tests conducted on two other separately collected soil samples indicated that this maximum retention capacity would be of the order of  $5 \times 10^4$  to  $1.5 \times 10^5$  kilograms per hectare. The soil sample with lower retention capacity was observed to contain a greater proportion of sandy materials.

It should be pointed out that the above calculated retention values are specific to a given disposed soil system and to a solution with specific ions. To determine the reduction in sorption capacity from the competing action of other ions in a disposed soil solution, 1000 mg of Ca ions were introduced into the same solution containing 1000 mg of Cd in 1000 mL of water. Figure 1 shows some reduction in the amount of Cd removed. However, the reduction caused by the addition of this competing species was only 10 percent; 90 percent of the Cd sorption was completed within a period of 12 hours.

#### Test Apparatus

Six flow units were constructed using polyvinyl chloride (PVC) pipes having a central cylinder 10 cm in length and 7.5 cm in internal diameter to hold the soil columns. The construction details of a typical flow unit are presented in Figure 2. The volumes of the anode and cathode reservoirs were approximately one liter each. Each reservoir was furnished with a drainage port and

flexible tubing for the removal of excess liquid. The copper electrodes were made from 1.6 mm thick plates with a surface area of 2.5 cm by 5.0 cm. An alternating current (AC)-to-DC converter was used as a power source. The saturated soil cores were subjected to a potential gradient through these copper electrodes. The increase or decrease in water volume in each reservoir was measured by observing the drop in water level in the riser columns or the amount of water removed through the drainage ports.

#### Hydraulic Conductivity Studies

Soil cores were prepared using air-dried Randall clay passed through a US No. 10 mesh sieve (1.651 cm). The cores were assembled in the apparatus as shown in Figure 2. The physical properties of these cores are presented in Table 2. After the pore air was purged by a flow of CO<sub>2</sub> over a period of 24 hours, the cores were saturated with distilled water. After saturation, the pH of the water in the anode and cathode reservoirs ranged between 6.2 and 6.75. The pH of tap water from the Lubbock Municipal System is typically above 8. The permeabilities of the original cores No. 1 and 4, conducted under a hydraulic gradient of 0.45 cm/cm, were  $5.1 \times 10^{-7}$  cm/s and  $7.3 \times 10^{-7}$  cm/s, respectively. Under unit hydraulic gradient, these values could be calculated to be  $1.1 \times 10^{-6}$  cm/s and  $1.6 \times 10^{-6}$  cm/s, respectively. Later, it was learned that these cores were not fully saturated. Soil core No. 4a had a porosity of 0.5 and a permeability of  $3.8 \times 10^{-5}$  cm/s under a hydraulic gradient of 2 cm/cm at the end of the test. As can be seen from Figure 3, the permeability of this core decreased with time in the 18-day test period. However, the permeability under a hydraulic gradient of 0.45 cm/cm remained essentially constant over the test period and averaged  $1.3 \times 10^{-5}$  cm/s. Thus, the hydraulic conductivity for this soil core under unit hydraulic gradient was estimated to range from  $1.9 \times 10^{-5}$  cm/s to  $2.9 \times 10^{-5}$  cm/s. Soil core No. 5a also showed a similar drop in permeability in a five-day test period. Under a hydraulic gradient of 0.45 cm/cm, the permeability remained constant with time; however, this core showed no improvement in permeability when subjected to a potential gradient of 0.15 V/cm (Figure 4). The hydraulic conductivity of this soil core under unit hydraulic gradient was of the order of  $1.1 \times 10^{-6}$  cm/s to  $1.8 \times 10^{-6}$  cm/s. It should be pointed

TABLE 2. PHYSICAL PROPERTIES OF SOIL CORES USED IN THE ELECTRO-OSMOSIS STUDY

Core No.	Volume (mL)	Bulk Density (g/cm <sup>3</sup> )	Porosity*	Pore Volume (mL)	Particle Density** (g/cm <sup>3</sup> )
Original Packing					
1	475.8	1.51	0.42	199	2.60
2	468.6	1.51	0.42	196	2.60
3	482.9	1.48	0.43	208	2.60
4	479.3	1.54	0.41	197	2.60
5	472.2	1.53	0.41	194	2.60
6	475.8	1.52	0.42	200	2.60
New Packing					
4a	468.6	1.29	0.50	234	2.60
5a	472.2	1.20	0.54	255	2.60
#					
1a#	475.8	1.47	0.45	214	2.65
3a	482.9	1.34	0.49	237	2.60
6a	475.8	1.20	0.54	257	2.60

\*Porosity =  $1 - (\text{bulk density}/\text{particle density})$

\*\*Assumed particle density

#Contained equal mixtures of Ottawa sand and Randall clay and the particle density was assumed to be slightly higher than the rest.

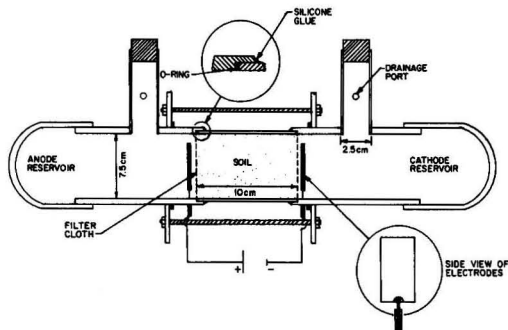


Figure 2. Schematic diagram of laboratory setup.

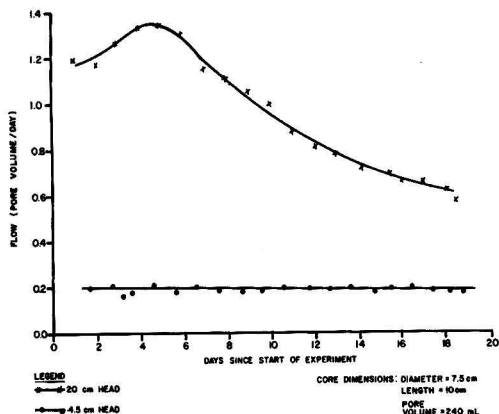


Figure 3. Saturated hydraulic conductivity of core no. 4a versus time.

### Salt Buildup and Backflow

The packed soil cores were allowed to operate under an imposed potential gradient of 0.15 V/cm. The anode reservoir contained a synthetic solution of NaCl, CaSO<sub>4</sub> and CdCl<sub>2</sub> with a total dissolved solids (TDS) concentration of 400 mg/L. The Cd concentration was of the order of 10.0 mg/L. The original core No. 2 produced a significant backflow after one month of operation at this potential gradient. It was discovered that the TDS of the water in the cathode reservoir was greater than 5000 mg/L. A buildup of salts in the cathode reservoir could reduce the thickness of the double layer and might eventually lead to a preponderance of the opposite charge [10]. This reversal of charge could produce a backflow thus reducing the effectiveness of the units. It was realized that a positive salt gradient should be maintained from the anode to the cathode side for electro-osmotic flow.

Flow unit No. 1 was tested with its original soil core without changing the ion concentration in the cathode reservoir to determine the ion gradient at which backflow could occur. At the beginning of the test, the TDS in the anode and cathode reservoirs were 700 mg/L and 100 mg/L, respectively. A backflow occurred after 11 days of operation at which time the TDS concentrations were 650 mg/L and 900 mg/L respectively.

It was speculated that ions were released from the soil core because of leaching. Several elutriate tests were conducted with various ratios of soil and water masses but the release of ions from the soils through leaching was insignificant. It was therefore concluded that the ion movement was mostly from the soil core to the cathode reservoir because of the electrical environment. No complete chemical analysis was performed on the water samples of the cathode reservoirs (after backflow production) to differentiate the species.

out here that the test fluid for core No. 5a was tap water, whereas, distilled water was used for other cores. Because of time and material constraints, further testing was not carried out.

### OPERATIONAL PROBLEMS

A number of operational problems, e.g. backflow of water from the cathode reservoir to the anode reservoir, frequent replacement of electrodes due to corrosion, and excessive use of electricity as a result of electrolysis of water were encountered in this study. Before presenting the final results, the following sections summarize the problems and the corrective measures taken.

### Electrolysis of Water

Electrolysis of water in the anode and cathode reservoirs was a major problem even at low voltage gradients. Casagrande [4] reported the optimum potential gradient for electro-osmosis to be 0.5 V/cm. During the course of this experiment, the potential gradient was maintained between 0.15 V/cm to 0.45 V/cm except for one occasion in which the potential gradient was approximately 1.0 V/cm. Electrolysis of water even at a potential gradient of 0.15 V/cm was noticeable because of the quantities of trapped gases observed in the reservoirs. At higher potential gradients, considerable energy is used to decompose the water molecules rather than being utilized for electro-osmosis. Thus, the cost effectiveness is low.

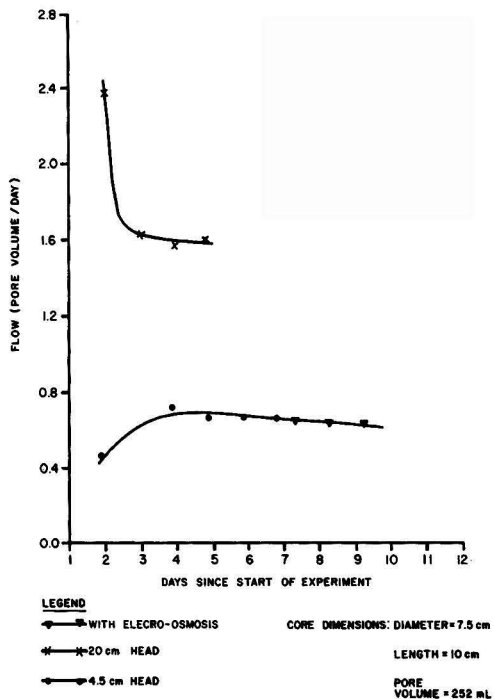


Figure 4. Saturated hydraulic conductivity of core no. 5a versus time.

### Electrode Conditions

The corrosion of anodes after a few months of operation of the flow units decreased the electro-osmotic flow. Severe pitting was observed on the removed electrodes. Similarly, thick crusts were formed over the cathodes. These crusts were likely caused by the reaction of copper with the carbonates and bicarbonates contained in the water. These conditions had necessitated the frequent replacement of electrodes.

### Soil Type and Bulk Density Effects on Flow

The bulk densities of originally packed soils were approximately 1.5 g/cm<sup>3</sup>. As mentioned earlier, many cores were not saturated at their centers. Additional cores with bulk densities ranging from 1.2 to 1.35 g/cm<sup>3</sup> were prepared to simulate observed in-situ properties. Although

the saturation was increased, no improvements in flow were observed. Kezdi [11] has suggested that if the soil pores were larger, a galvanic process causing electrolysis would be prominent and the electric current passing through the soil could no longer be used for drainage by electro-osmosis. Soil cores prepared from a mixture of Ottawa sand and Randall clay (50% each and having a bulk density of the order of 1.4 g/cm<sup>3</sup>) produced less flow than similarly packed cores of Randall clay alone under similar potential gradients.

## CORRECTIVE MEASURES AND FINAL RESULTS

To investigate the effective positioning and orientation of electrodes, two additional pairs of electrodes were inserted into soil cores No. 1a and 3a at distances of 2.5 cm from the edges. These electrodes were installed vertically upside down. The flow units were operated by imposing electric potentials through the four electrodes simultaneously. However, no improvement in rate of flow was observed.

The energy requirement to drain one cubic meter of water for flow unit No. 2 was estimated to be  $7.56 \times 10^5$  kJ. Considering the effect of backflow, the overall energy requirement would be about  $1.08 \times 10^6$  kJ per m<sup>3</sup> of drained water.

The flow unit that contained Core No. 5a was estimated to require  $1.44 \times 10^5$  kJ to drain one cubic meter of water in the first 15 days of operation neglecting the effect of backflow. The energy requirement would be about  $2.45 \times 10^5$  kJ if the backflow effects were to be considered. The rate of energy consumption increased to  $8.1 \times 10^5$  kJ per cubic meter of drained water in the next 12 days of study. Based upon the results of this 27-day study, it was estimated that about 225 days would be required to remove one pore volume of water by means of electro-osmosis. Under unit hydraulic gradient, the permeability of this core would range from  $1.4 \times 10^{-6}$  cm/s to  $2.1 \times 10^{-6}$  cm/s, thus indicating a 15 to 20 percent increase in average flow.

A reversal of polarity was utilized on some flow units in an attempt to save the corroding anodes. However, the coated cathode which became the new anode was not effective in producing an electro-osmotic flow in a flow unit operated at a potential gradient of 1.0 V/cm for about 10 days. The energy requirement in this test period was estimated to be  $4.68 \times 10^6$  kJ per cubic meter of water drained. Only 0.11 pore volume of water passed through the soil core during this 10-day test period.

## CONCLUSIONS AND SUGGESTIONS

The results of this study indicated that Randall clay possesses a high sorption capacity for heavy metals like Cd, Cu and Pb. This soil can handle a high hydraulic loading of wastewater before it becomes saturated with heavy metals and other ions.

Preliminary data indicated that clay permeability could be improved by electro-osmosis. However, electro-osmosis was energy intensive and the time required to pass one pore volume of water through these clay soils was high. The loss of energy through electrolysis of water could become a major expense if flow units were to be operated under high potential gradient.

In addition, the corrosion of anodes and the coating of cathodes necessary for establishing the electrical environment could pose operational and maintenance problems. The salinity of the external electrolyte (test fluid) may also affect flow. A positive salinity gradient should be maintained in the test fluid in the direction of fluid flow to avoid backflow effects.

Future research should be directed toward improving techniques that could reduce energy requirements in operation. An energy-efficient electrode system should be devised and configured on a bench-scale system.

## LITERATURE CITED

1. Jumikis, A. R., "Soil Mechanics," p. 222-224. Van Nostrand Co., Inc., Princeton, N.J. (1962).
2. Taylor, S. A., "Physical Edaphology — The Physics of Irrigated and Nonirrigated Soils," Chapter 5, p. 95-124, W. H. Freeman Co., San Francisco (1972).
3. Vey, E., "Geotechniques and Geotechnical Research," Proceedings, 29th Annual Meeting of Highway Research Board, Washington, D.C., p. 578-589 (1949).
4. Casagrande, L., "Electro-osmosis in Soils," *Geotechnique*, Vol. 1, No. 1, p. 1959-1977 (1949).
5. Preece, E. F., "Geotechniques and Geotechnical Research," Proceedings, 27th Annual Meeting of Highway Research Board, Washington, D.C., p. 384-416 (1947).
6. Gray, D. H., "Electro-chemical Hardening of Clay Soils," *Geotechnique*, Vol. 20, No. 1, p. 81-93 (1970).
7. Peterson, J., "Electro-osmosis: a Review of Recent Field Experience," in N. J. McClelland, Ed. Proceedings of Sixth National Conference, National Sanitary Foundation, 1979, p. 477-492, Ann Arbor Science, Ann Arbor, Mich. (1980).
8. Coolbroth, F. P., "The Sewage Osmosis Concept for on-site Disposal Systems — Clay Soils," in N. J. McClelland, Ed. Proceedings of Third National Conference, National Sanitary Foundation, 1976, p. 131-137, Ann Arbor Science, Ann Arbor, Mich. (1977).
9. Smith, D. L. O., "A Laboratory Evaluation of the Sewage Osmosis Concept," M. S. Thesis, Iowa State University, Ames, Iowa (1978).
10. Gray, D. H. and J. K. Mitchell, "Fundamental Aspects of Electro-osmosis in Soils," *J. Soil Mech. Found. Div. Proc. ASCE*, Vol. 93, No. 6, p. 209-236 (1967).
11. Kezdi, A., "Handbook of Soil Mechanics," Vol. 1 (Soil Physics), p. 178-181. Elsevier Scientific Publishing Co., Amsterdam (1974).



Chittaranjan Ray is currently employed by Geraghty & Miller, Inc. as an Engineer in their Hackensack office. During the conduct of this study, he was a Graduate Student in the Department of Civil Engineering, Texas Tech University.



R. H. Ramsey is Associate Professor of Civil Engineering, Texas Tech University, Lubbock, Texas. He is active in the areas of land application of municipal wastewater, subsurface drip irrigation, and water quality impacts of groundwater recharge through Playa lakes. His primary research interests are in the area of water and solute transport in unsaturated zone. He has published 32 papers and has prepared a number of reports and holds a Ph.D. degree from the University of Oklahoma. He is a member of American Society of Civil Engineers and is also a registered professional Engineer in the State of Texas.

# Adsorption of Inorganic Arsenic and Organoarsenicals on Hydrous Oxides

Mriganka M. Ghosh

The Pennsylvania State University, University Park, PA 16802

Jill R. Yuan

The National Chung Hsing University, Taichung, Taiwan

*Adsorption of aqueous arsenic on activated alumina was investigated. pH greatly affects the surface chemical interactions of all species of arsenic, inorganic or organic, with hydrous alumina. Arsenate adsorbs well at pHs less than the  $pH_{zpc}$  of alumina, with maximum adsorption occurring at pH 5. Maximum adsorption of arsenite occurs at pH 8. The adsorption behavior of monomethyl arsonate (MMA) is similar to that of arsenate. Adsorption of arsenic is enhanced by the presence of cations. Experiments with fixed alumina beds with an empty bed contact time (EBCT) of only five minutes or less indicate that arsenic concentrations typical of North American waters can be removed effectively for long periods of time without regeneration. Spent alumina beds can be successfully regenerated using 0.5% NaOH followed by dilute acid rinse.*

## INTRODUCTION

Arsenic is a commonly occurring toxic element that is federally controlled not to exceed 0.5 mg/l in drinking water. The health effects of arsenic are fairly well documented [1]. Arsenic naturally occurs in areas of high geothermal activity. However, smelting, petroleum-refining and herbicide manufacturing may introduce significant quantities of arsenic to the environment locally. Contamination of ground water by leachate from land disposal of arsenical wastes has also been reported [2]. In a study of subsurface migration of organic and inorganic arsenic in an abandoned herbicide manufacturing plant, a total arsenic concentration of 900 mg/l was recorded at a depth of 35 feet of sand underlain with a 50 foot clay layer [3]. The vertical mobility depends on speciation and the type of soil. Before they are metabolized by soil bacteria, organoarsenicals may form surface complexes with oxides on soil surfaces that are relatively more soluble than their inorganic counterparts. Microbial methylation of arsenic progresses sequentially to monomethyl arsonate (MAA), cacodylic acid (CA), and trimethyl arsine oxide (TMAO). Eventually, however, all forms of organoarsenicals are believed to form arsenate in soil, possibly by demethylation. Seemingly, biomagnification of arsenic along the

food chain does not occur [4]. The toxicity scale of arsenic is as follows [5]:

arsine > arsenite > arsenate > alkyl arsenic

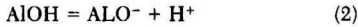
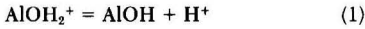
Arsenic is stable in four oxidation states (+V, +III, 0, -III) under different redox conditions. In oxygenated waters, arsenate species ( $H_2AsO_4^-$ ,  $HAsO_4^-$ , and  $AsO_4^-$ ) are stable. At Eh values characteristic of mildly reducing conditions, arsenite species ( $H_3AsO_3$ ,  $H_2AsO_3^-$  and  $HAsO_3^{2-}$ ) become stable [6]. The pK values for  $H_3AsO_4$  at 25°C are 2.2, 6.98, and 11.55 and those for  $H_3AsO_3$  are 9.22, 12.13, and 13.4. Hydroxides of iron, chromium and aluminum strongly adsorb or form insoluble precipitates with arsenites and arsenates. This may play an important role in controlling arsenic concentration in unpolluted waters. In the presence of sulfides, realgar ( $As_2S_3$ ) and orpiment ( $As_2S_3$ ) may be present as stable solids at pH less than about 5.5 and Eh of about 0 volts.  $HAsS_2$  and  $AsS_2^-$  are the predominant aqueous species. Under extremely reducing conditions, arsine may occur in traces being only slightly soluble ( $10^{-5.3}$  M at  $P_{AsH_3} = 1$  atm). The most commonly used forms of methylated arsenic that are used in herbicides are  $CH_3AsO(OH)_2$  (MAA) and  $(CH_3)_2ASO_2H$  (CA). They are both highly soluble in water. MMA has pK values 4.19 and 8.77 at 25°C and the pK for CA is 6.27.

Many methods have been used to remove arsenic from aqueous solutions, both under laboratory and field conditions. Precipitation with lime and ferric salts followed by adsorption onto the resultant floc is most common [7-9]. Sulfide precipitation [10], adsorption on activated carbon [10, 11], and adsorption on activated alumina [12-14] have also been used for removing arsenic. Ion exchange has been used with some success [10, 15].

This paper deals with a study of the kinetics of arsenic removal by alumina qualitatively, establishes removal capacities of alumina, and explores the feasibility of regenerating spent alumina in an effort to evaluate process economics.

## SURFACE REACTIONS

The surface hydroxy groups formed at the water-alumina interface behave amphotericly as shown:



where  $\text{AlOH}_2^+$ ,  $\text{AlOH}$  and  $\text{AlO}^-$  are protonated, neutral and deprotonated surface hydroxy groups. The intrinsic surface acidity constants give free energy of the deprotonation process shown in Equations 3 and 4 below:

$$K_{a1}^{\text{int}} = \frac{\{\text{AlOH}\}\{\text{H}^+\}}{\{\text{AlOH}_2^+\}} \quad (3)$$

$$K_{a2}^{\text{int}} = \frac{\{\text{AlO}^-\}\{\text{H}^+\}}{\{\text{AlOH}\}} \quad (4)$$

The total number of surface sites, a measure of the acidity capacity, can be calculated from the sum of the concentrations of surface hydroxy groups:

$$N_t = \{\text{AlOH}_2^+\} + \{\text{AlOH}\} + \{\text{AlO}^-\} \quad (5)$$

Alkalimetric titration may be used to calculate the surface acidity (Equation 5) and surface acidity constants (Equations 3 and 4) of hydrous oxides [16]. In Equation 5, at  $\text{pH} < \text{pH}_{\text{zpc}}$ ,  $N_t$  is approximately equal to the sum of the first two terms, and  $\text{pH} > \text{pH}_{\text{zpc}}$ ,  $N_t$  is equal to the sum of the last two terms. The terms  $\{\text{AlOH}_2^+\}$  and  $\{\text{AlO}^-\}$  are equal to  $[\text{X}^+]$  and  $[\text{X}^-]$ , respectively, where X represents an estimate of charge density, positive or negative. Equations 3 and 4 can be rearranged as follows:

$$\frac{1}{\{\text{H}^+\}} = \left( \frac{N_t}{K_{a1}^{\text{int}}[\text{X}^+]} \right) - \frac{1}{K_{a1}^{\text{int}}}; \text{ at } \text{pH} < \text{pH}_{\text{zpc}} \quad (6)$$

$$\{\text{H}^+\} = \frac{N_t K_{a1}^{\text{int}}}{[\text{X}^-]} - K_{a2}^{\text{int}}; \text{ at } \text{pH} > \text{pH}_{\text{zpc}} \quad (7)$$

The surface concentration of hydrogen ion,  $\{\text{H}^+\}$ , can be calculated from pH of the bulk solution and surface potential,  $\psi_0$ :

$$\{\text{H}^+\} = [\text{H}^+] \exp(-F\psi_0/RT) \quad (8)$$

where F, R, and T are Faraday constant, gas constant, and absolute temperature, respectively. An indirect estimate of surface potential can be obtained from zeta potential, i.e., from the zero point of charge,  $\text{pH}_{\text{zpc}}$ :

$$\psi_0 = \frac{2.303RT}{F} (\text{pH} - \text{pH}_{\text{zpc}}) \quad (9)$$

The surface potential can also be estimated from the theory of electrical double layer (EDL). For a 1:1 electrolyte at 25°C, the surface potential and charge density are approximately related as shown in Equation 10 for solu-

TABLE 1. CHARACTERISTICS OF COMMERCIAL ACTIVATED ALUMINA

$\text{Al}_2\text{O}_3$	92.2%
$\text{Na}_2\text{O}$	0.9%
$\text{Fe}_2\text{O}_3$	0.08%
Loss in ignition	6.5%
BET surface area (28 × 48 mesh alumina)	218 m <sup>2</sup> /g
Intrinsic acidity constants (I = 0.1 M; temperature = 20°C)	
$K_{a1}^{\text{int}} = 6.44$	
$K_{a2}^{\text{int}} = 9.4$	
$\text{pH}_{\text{zpc}} = 7.92$	
$N_t = 4.6 \times 10^{14}$ sites/cm <sup>2</sup>	

tions of low ionic strengths where the effects of Stern layer can be ignored:

$$\psi_0 = 51.4 \sinh^{-1} \left\{ (1/11.7I^{0.5})\sigma_0 \right\} \quad (10)$$

where  $\psi_0$ , I and  $\sigma_0$  are expressed in mV, M and  $\mu\text{C}/\text{cm}^2$ , respectively [17]. The surface charge density,  $\sigma_0$ , can be calculated from the results of alkalimetric titration:

$$\sigma_0 = F(\Gamma_{\text{H}} - \Gamma_{\text{OH}}) \quad (11)$$

where  $(\Gamma_{\text{H}} - \Gamma_{\text{OH}})$  is the adsorption density of the potential determining ion relative to adsorption at  $\text{pH}_{\text{zpc}}$ . The intrinsic acidity coefficients and capacity can be calculated from linear plots of Equations 6 and 7.

## MATERIALS AND METHODS

### Activated Alumina

All adsorption experiments were conducted using a commercial grade activated alumina ( $\gamma\text{-Al}_2\text{O}_3$ ). It contained 92 percent  $\text{Al}_2\text{O}_3$  and some minor impurities. The average BET surface area for 28 × 48 mesh as measured using Qantasorb surface area analyzer was 218 m<sup>2</sup>/g. The complete characteristics of the alumina used are given in Table 1. The intrinsic acidity constants, surface site concentration, and zeta potential of the virgin alumina are also shown in this table. The test alumina for any adsorption experiment was prepared by washing it with 0.01N NaOH solution and rinsing with deionized water (DI) till the pH and conductivity of the supernatant became constant. It was then dried overnight at 105°C before use.

### Alkalimetric Titration

The test alumina suspensions were prepared by suspending prewashed alumina (2 gm/l), aged for two weeks in contact with DI water, in stock NaCl solution so that final ionic strength of  $10^{-3}$  M was obtained. The titrants used were 0.1 M HCl of 0.1 M NaOH. Approximately ten different titrant volumes, each for acid and alkali, were used to obtain titration curves. Bottles containing 2 g/l of alumina at an ionic strength of  $10^{-3}$  M and preselected volumes of titrants were mixed for 24 hours in a rotary shaker and the final suspension pH measured. Additional concentrated NaCl was added to each bottle to raise ionic strength to  $3 \times 10^{-3}$  M and the entire titration process was repeated. Titrations were carried out at ionic strengths of  $10^{-3}$ ,  $3 \times 10^{-3}$ ,  $10^{-2}$ , and  $10^{-1}$  M. Blank titrations of 2 g/l alumina suspensions preaged for 24 hours at identical ionic strengths were carried out on filtered supernatants. The titrant volumes for blank titrations were subtracted from those for alumina suspensions to obtain net titration for the alumina surface. The surface charge,  $\sigma_0$ , was computed as follows:

$$\sigma_0 = F (Mv_1)/(VC_aS) \quad (12)$$

where F = Faraday constant (coul/mole); M = concentration of acid or base (mole/l);  $v_1$  = net amount of acid or

base used (ml);  $V$  = volume of sample (ml);  $C_a$  = concentration of activated alumina (g/l);  $S$  = specific surface area of alumina ( $m^2/g$ ).

### Equilibrium Adsorption Experiments

All adsorption isotherms were obtained using batch adsorption experiments. Predetermined amounts of washed alumina (1 to 5 g/l) were placed in 150 ml plastic bottles. The ionic strength in all bottles were maintained at  $1 \times 10^{-1}$  M with NaCl and the final sample volume was adjusted to 125 ml. The concentration of sorbate was varied from 1 to 20 mM depending on the arsenic species being adsorbed. The pH was adjusted using strong acid (1 N HCl) or strong base (1 N NaOH). The bottles were continuously shaken for seven days at room temperature ( $22^\circ C \pm 1^\circ C$ ) for attainment of equilibrium. To determine kinetics of removal, samples were removed at specified time intervals, pH measured, filtered through 0.45  $\mu m$  Millipore filter, and arsenic concentration in the filtrate determined using atomic absorption spectrophotometry following hydride reduction of arsenic.

### Column Studies

The studies for fixed bed adsorption of arsenic on alumina were conducted by passing arsenic solution through 0.9 cm diameter, 76 cm long glass minicolumns containing alumina supported by glass wool. Different amounts of alumina (1 to 5 g) were used to vary the empty bed contact time (EBCT) in different experiments. The columns were fed arsenic solution from a 20-1 Nalgene carboy, the flow rate through the column being held constant by peristaltic pumps on the effluent end. A blank column containing no alumina was also run to determine loss due to adsorption on column wall. Arsenic loading on alumina was calculated from the total weight of arsenic removed per unit weight of alumina used in the column. This was obtained from the difference in concentration between influent and the total effluent volume collected during a given experiment. Generally, an experimental run was terminated when the adsorption capacity of alumina was exhausted, that is, when effluent concentration of arsenic equalled that in the influent. In certain cases, column runs were terminated if no arsenic breakthrough occurred for a prolong period (more than 30 days).

Regeneration of spent alumina was performed by using NaOH solutions of varying strengths initially, 0.5%, 1% and 3%, to determine optimum regenerant concentration based on alumina loss and restored bed capacity. A concentration of 0.5% was used for most runs thereafter. Hydraulic rates ranging from 68-79  $m^3/m^2 \cdot d$  were used in an upflow mode to apply regenerant chemicals. Sixty to eighty bed volumes (BV) of caustic solution followed by 10-15 BV of 0.1% HCl and 15-20 BV of DI water were used for regeneration.

## RESULTS AND DISCUSSION

### Surface Acidity of Alumina

The surface charge density distribution as a function of pH, shown in Figure 1, was obtained using Equations 11 and 12. The  $pH_{zpc}$  of the commercial alumina was found to be 7.92. This value may vary depending on the origin, aging, doping by impurities, and the degree of hydration of alumina. Values in the range 7.4 to 8.6 for  $\gamma-Al_2O_3$  have been reported. Although the alumina surface can be treated as a diprotic acid, the acidity of each surface group is affected by the neighboring group. The two intrinsic acidity constants for the test alumina were determined in

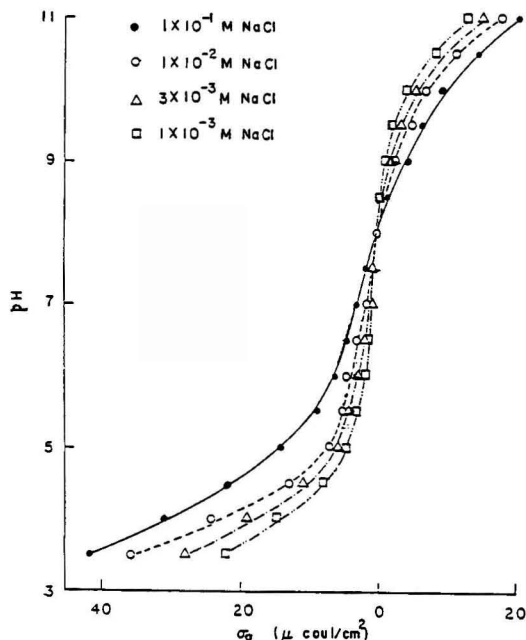


Figure 1. Surface charge distribution on alumina.

accordance with Equations 6 and 7, as shown in Figure 2. The constants were calculated to be 6.44 and 9.4 at an ionic strength of  $1 \times 10^{-1}$  M. The total number of exchangeable sites,  $N_t$ , was found to be 1.67 mmoles/g or  $4.6 \times 10^{14}/cm^2$ . This number is about six times higher than

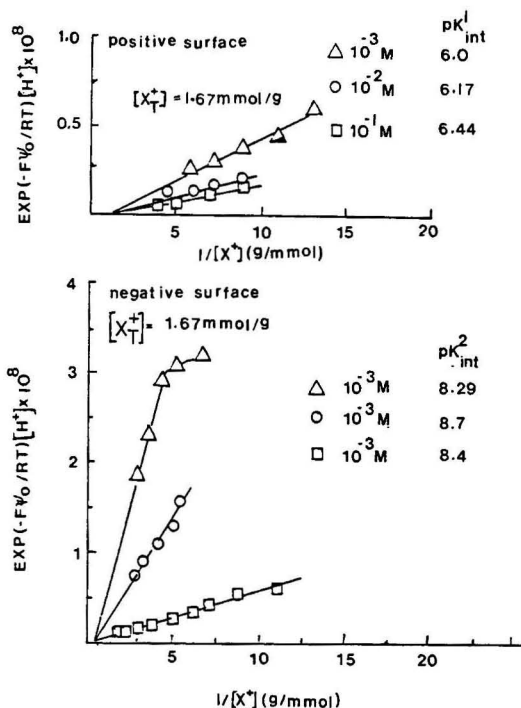


Figure 2. Graphical determination of intrinsic acidity constants.

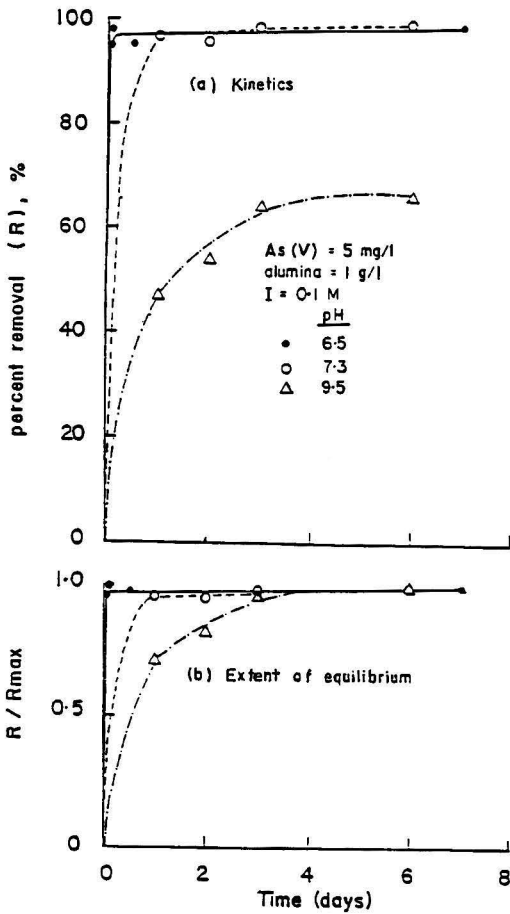


Figure 3. Effect of pH on arsenate adsorption (temperature = 20°C).

the one reported by Huang [18] but close to the value reported by Davis [19]. This method works well at high ionic strengths used in this study. A  $pH_{zpc}$  of 7.92, which is the same obtained from Figure 1, was determined analytically by taking the average of the two acidity constants.

**Removal Kinetics**

Typical kinetic data for the adsorption of arsenate on activated alumina are shown in Figure 3. The removal was rapid in the first 24 hours and then slowed considerably as the reaction approached equilibrium. At a pH of 6.5 or higher, 95 percent of the maximum removal was obtained in less than 24 hours. At a surface loading of 67  $\mu\text{mole/g}$ , arsenate concentration decreased from 5 mg/l to 0.1 mg/l in a few hours in the pH range of 6 to 7. At a pH of 9.5, arsenate concentration decreased to only 1.75 mg/l even after 6 days. At similar surface loadings on the same alumina, Rosenblum and Clifford [14] reported a decrease of arsenate from 5 mg/l to 0.75 mg/l in about 12 hours and to 0.5 mg/l in 6 days, at a pH of 8. The presence of much higher total dissolved solids (TDS = 1067 mg/l) in the latter case may account for the slight difference in results. The high degree of removal at low pH levels imply that the adsorption may be non-specific. Chemical adsorption is usually slower than coulombic or physical processes owing to the fact that it may be site specific and

ligand orientation may be necessary. Although specific chemical adsorption cannot be ruled out altogether, apparently coulombic or physical processes play a significant role in arsenate adsorption at low pH levels. At  $pH < pH_{zpc}$ , the alumina surface is positively charged and coulombic interaction with arsenate is feasible. At  $pH > pH_{zpc}$ , the surface carries a net negative charge. Adsorption at these pHs must occur by specific adsorption in spite of any coulombic repulsion.

The effects of temperature and ionic strength on the adsorption of arsenate are shown in Figures 4 and 5, respectively. The results for Figure 4 were obtained at pH 8.6 and an ionic strength of  $1 \times 10^{-1}$  M, while the data for Figure 5 were obtained at a temperature of 20°C. A pH of 8.6 was selected to slow down the rate of adsorption during the first two days. In all experiments the concentrations of alumina and arsenate were held constant. At 20°C or higher, the rate of adsorption remained essentially unchanged. Based on the results presented in Figures 3 and 4, equilibrium adsorption was assumed to occur at 6 days regardless of temperature and pH. Ionic strength had no effect on adsorption within the range of values studied.

Arsenite exhibited a different adsorption behavior (Figure 6). Maximum removal occurred at approximately pH 8 regardless of the initial surface loading. However, the rate of approach to equilibrium was much slower than that for arsenate, although a two-step removal, similar to that for arsenate, was observed. Similar results for the adsorption of arsenite on amorphous  $\text{Fe}(\text{OH})_3$  have been reported by Pierce and Moore [20].

Although a quantitative analysis of the kinetic data was not performed, the adsorption of the anions studied can

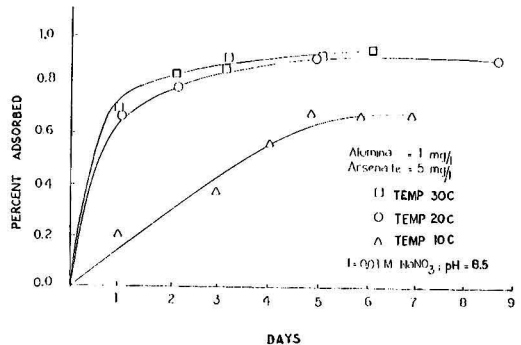


Figure 4. Effect of temperature on arsenate adsorption (alumina = 1 g/l; As(V) = 5 mg/l; temperature = 20°C).

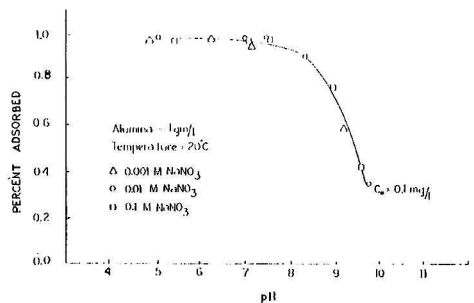


Figure 5. Effect of ionic strength on arsenate adsorption (alumina = 1 g/l; As(V) = 5 mg/l; temperature = 20°C).

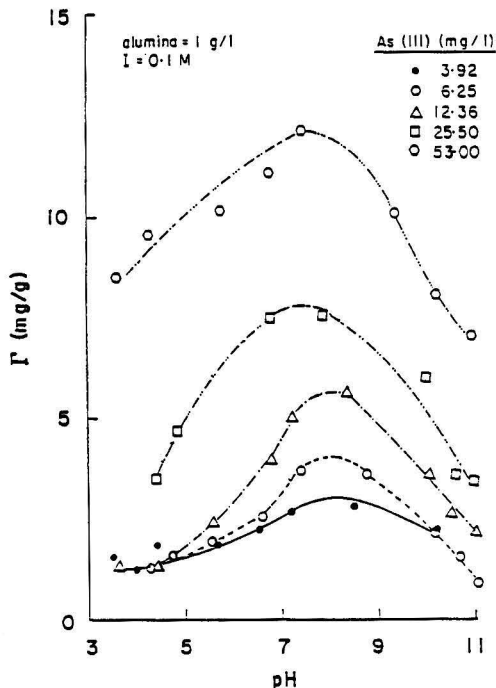


Figure 6. Effect of pH and adsorbate concentration on adsorption of arsenite.

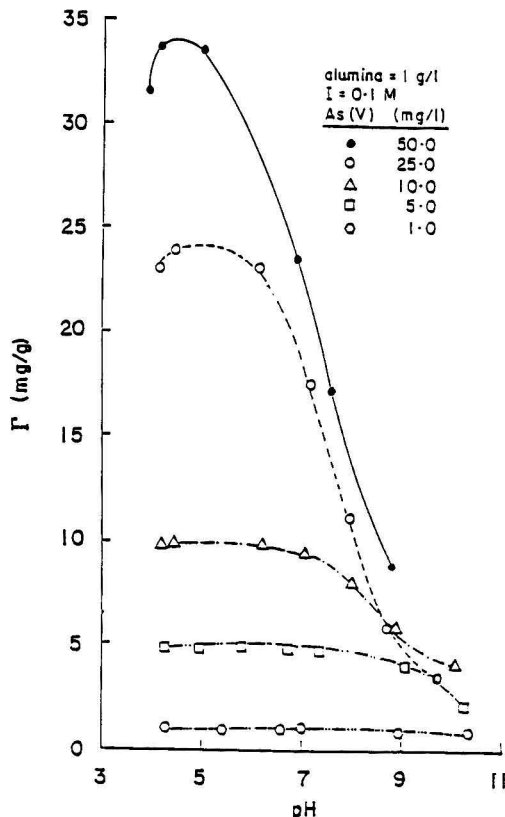


Figure 7. Effect of pH and adsorbate concentration on adsorption of arsenate.

be treated as a diffusion-controlled reaction and therefore it is transport-limited. The reaction of anions that form surface complexes cannot be explained by simple ion exchange on an equivalent basis as in the non-specific exchange of  $\text{NO}_3^-$  or  $\text{Cl}^-$ . In specific adsorption the surface coverage varies with ionic species, pH, and the presence of other specifically adsorbable ions.

#### Equilibrium Adsorption

In many instances, specific adsorption of anions can be described adequately by the well known Langmuir isotherm focusing only on the surface reactions. Assuming that the surface charge on the adsorbent remains constant, an isotherm can be derived for ligand adsorption using the definition of surface complex formation coefficients:

$$SA^{(z-1)} = \frac{N_i K_i A^z}{1 + K_i A^z} \quad (13)$$

$$K_i = \frac{K_i^s a_i^s}{(\text{OH})^-} \quad (14)$$

where  $K_i^s$  is the complexation constant for the adsorption of  $A^z$ ,  $a_i^s$  is the fraction of  $N_i$  present as unprotonated surface oxide,  $\text{SOH}$ , and  $K_i$  is the adsorption equilibrium constant at constant pH. The applicability of this result in describing adsorption of a single ligand has been confirmed by many researchers [21, 22]. Considering adsorption to be a coordinative reaction of 1:1 stoichiometry between concentration of adsorption sites and that of the adsorbate, Equation 13 reduces to the well known form of the Langmuir equation:

$$\Gamma = \frac{\Gamma_m K_i C}{1 + K_i C} \quad (15)$$

where  $\Gamma$  is adsorption density (mol/g or mg/g),  $C$  is the equilibrium concentration of solute in solution, and  $\Gamma_m$  is the maximum adsorption density for monolayer coverage. Typical data for the adsorption of arsenate are shown in Figure 7. The initial concentration of arsenic was varied from 0.013 to 0.7 mM in these experiments while the amount of adsorbate was held constant. At high alumina to arsenic ratios, the dependence of adsorption on pH is masked. In fact, at such high adsorbent concentrations, the pH effect becomes insignificant. Except at high concentrations, adsorption appears to be independent of pH at  $\text{pH} < \text{pH}_{zpc}$  and decreased with increasing pH. At increased initial surface loadings, the optimum pH of adsorption decreases due to a lowering of  $\text{pH}_{zpc}$ . In the pH range of 3 to 6,  $\text{H}_2\text{AsO}_4^-$  is the predominant species, and, apparently, the major species being adsorbed. In this pH range alumina surface acquires a net positive charge and

TABLE 2. LANGMUIR CONSTANTS FOR ADSORPTION OF ARSENIC (TEMPERATURE = 20°C; I = 0.1 M)

	pH	As(V)	MMA	DMAA
$\Gamma_m$ (mmol/g):	5.0	0.32	0.2	0.04
	6.5	0.28	0.22	0.0031
	7.5	0.15	0.14	0.0027
$K_i$ (l/mmol):	5.0	112	56	7
	6.5	96	20	21
	7.5	83	16	9



adsorption is facilitated by coulombic interactions. Hingson [23] suggested that the optimum pH for anion adsorption depends on the pK of the corresponding weak acid. However, for arsenate adsorption, optimum pH was almost 2 units lower than the pK<sub>2</sub> (6.98) of H<sub>3</sub>AsO<sub>4</sub>. The adsorption of arsenite increased to a maximum at pH 8 and then decreased with increasing pH (Figure 6). Gupta and Chen [12] observed only slight variations in the adsorption of As(III) in the pH range of 4 to 9 with a sudden drop above pH 9. Frost et al. [24] observed an increase in As(III) adsorption on kaolin in the pH range of 3 to 9. The adsorption of arsenate as a function pH is shown in Figure 7. The adsorption of arsenate, MMA and DMAA can be described by the Langmuir isotherm but the data for

arsenite adsorption do not fit Langmuir isotherm well. Table 2 gives the constants for Langmuir isotherm for the three adsorbates.

### Surface Complexation of Arsenate

Specific adsorption at pHs higher than the pH<sub>ZPC</sub> of the adsorbent is possible only if the undissociated acid gives a proton to the hydroxyl group on the surface to form H<sub>2</sub>O that can be readily displaced by the anion [24]. Adsorption may also be achieved on charged surfaces by electrostatic interactions where the EDL determines the extent of adsorption [25, 26]. Considering the pK values of H<sub>3</sub>AsO<sub>4</sub>, the predominant species in the pH range of 4 to 9 are H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and HAsO<sub>4</sub><sup>2-</sup>. Several surface complexes were considered for these two species. Values of the surface complexation constants were calculated from the surface loading and solution concentration of As(V), pH and adsorbent concentration. None of the complexation equilibria yielded a good fit of experimental data although the following models resulted in acceptable fit of experimental data:



The titration of alumina suspensions with or without the presence of arsenate and its conjugate acids are shown in Figure 8. The shift in the titration curves is caused by the release of OH<sup>-</sup> groups from the surface and the protonation-deprotonation reactions of arsenate. The variation of surface charge as a result of adsorption is shown in Figure 9. Adsorption of arsenate caused a significant reduction in the surface charge of alumina. The IEP shifted from 7.6 to 3.0 at an initial As concentration of 5 × 10<sup>-4</sup> M and an alumina concentration of 0.5 mg/l.

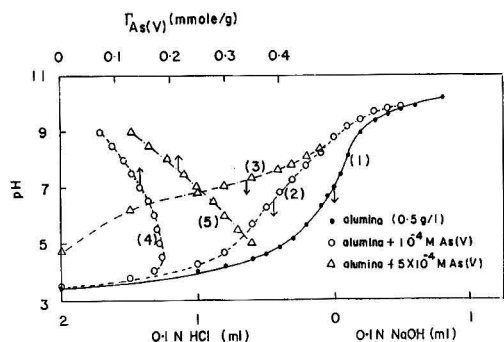


Figure 8. Titration of alumina suspension in the presence of arsenate (curves 1, 2, and 3) and corresponding adsorption densities.

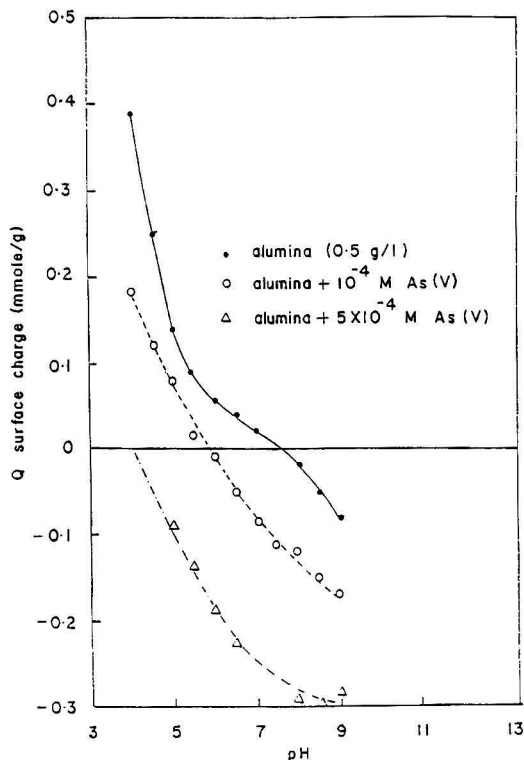


Figure 9. Specific surface charge on alumina following arsenate adsorption.

### Adsorption in Fixed Beds of Alumina

Fixed bed adsorbents were used to evaluate the effects of operational parameters, such as empty bed contact time (EBCT) and mass loading rate (MLR). The effect of MLR is shown in Figure 10 for an EBCT of 5 min and a pH of 6.5. As the effluent history profiles indicate, MLR is a significant factor in determining the life of an adsorption bed. At an initial concentration of 0.08 mg/l (1.1 × 10<sup>-3</sup> mM), typical of many natural waters, 30,000 BV could be treated before arsenic breakthrough occurred. Columns were operated at EBCTs of 3, 5 and 8 minutes, all receiving an As(V) concentration of 5.3 × 10<sup>-3</sup> mM at

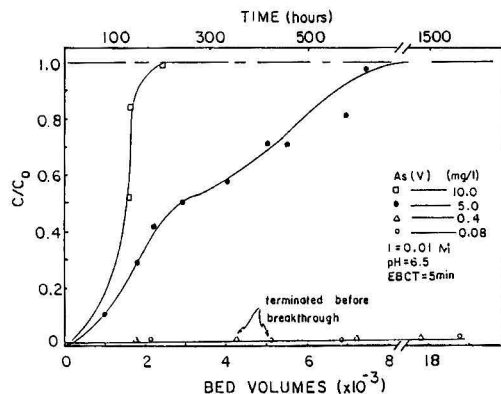


Figure 10. Effect of mass loading rate on adsorption of arsenate in fixed alumina beds.

TABLE 3. REGENERATION STUDIES

Influent conc. during adsorption (mg/l)	Total As adsorbed (mg)	Regenerant (%NaOH)	Acid Rinse (%HCl)	As desorbed		Throughput volume (l)	Alumina loss (%)
				(mg)	(%)		
<b>As(V)</b>							
10.0	148.25	3.0	1.0	148	100	5.95	5.6
2nd cycle 10.0	141.50						
	143.72	3.0	—	113	79	6.18	5.9
2nd cycle 2.0	96.80						
	126.50	3.0	0.1	111	88	5.59	5.7
2.0	121.60	1.0	0.1	102	84	5.20	4.2
2.0	100.20	0.5	0.1	99	99	4.78	3.4
2nd cycle 2.0	100	0.5	0.1	96	96	4.93	3.4
3rd cycle As(III)	98						
5.0	54.56	0.5	—	30	55	6.71	3.8
0.4	11.24	3.0	1.0	9	79	6.85	3.6

Rinse after regeneration consists of 10 to 15 BV of acid followed by 15 to 20 BV of deionized water. Regeneration rates range from 68 to 79 m/day.

pH 6.5. All columns could be operated for 1500 hours or longer. An EBCT of 3 minutes or longer was needed for satisfactory removal.

The economics of adsorption processes depend largely on the ability to rejuvenate spent beds. Reportedly, NaOH works well for desorbing arsenic from alumina [13]. Limited studies were made to determine the optimum concentration of NaOH which would produce good desorption without a large loss of alumina. As Table 3 indicates, spent alumina beds could be successfully regenerated using dilute solutions of NaOH followed by rinsing with dilute HCl and, finally, with deionized water. Excellent arsenic recovery could be accomplished using 0.5 percent NaOH solution. A total of 50-60 BV of caustic solution followed by 10-15 BV of acid solution were needed to obtain nearly complete desorption of arsenate. The loss of alumina was about 3 percent per regeneration cycle. The loss in adsorption capacity was negligible even after several regenerations (Figure 11).

SUMMARY AND CONCLUSIONS

Adsorption of arsenic on activated alumina is greatly affected by pH. High adsorption densities of arsenate and organoarsenicals can be obtained at pH  $pH_{zpc}$ . Maximum adsorption of arsenate occurs at pH 5 or less. The specific adsorption of arsenate, MAA and DMAA can be described well by Langmuir isotherm. Although no satisfactory fit of arsenate adsorption data to surface complexation models examined could be obtained, it appears that, in the pH range of 4 to 8,  $H_2AsO_4^-$  and  $HAsO_4^{2-}$  are the predominant species being adsorbed. Both coulombic and specific chemical interactions seem to be involved in the adsorption of arsenate. Arsenite adsorbs poorly on alumina. MAA and DMAA, two principal ingredients of most herbicides manufactured in the United States, are removed well by alumina. However, of these, MMA seems to be better adsorbed.

Experiments with fixed beds of alumina indicate that arsenic can be effectively removed for long periods of time at an EBCT of 3 minutes or longer and at relatively low MLRs, in the pH range of 4 to 7. Results also indicate that removal is best accomplished in the arsenate form. Therefore, oxidation of arsenite to arsenate may be necessary. Successful regeneration of spent alumina beds to desorb arsenate is feasible with NaOH at concentrations as low as 0.5 percent; but a much stronger caustic solution (3%) is needed for arsenite desorption. No appreciable loss in adsorption capacity occurs due to regeneration. The loss of alumina can be held at about 3 percent per regeneration.

ACKNOWLEDGMENTS

This study was funded by a research grant from the Office of Research and Development, U.S. EPA, Grant No. R 809425010. Mention of trade names in the paper does not constitute endorsement either by the author or EPA. The authors would like to thank Ron J. Schlicher, and Robert S. Teoh, who were involved with different phases of this study, and Don Carey of the U.S. EPA. A major portion of the results presented here was included in the Proceedings of the International Symposium on Metal Speciation, Separation and Recovery sponsored by

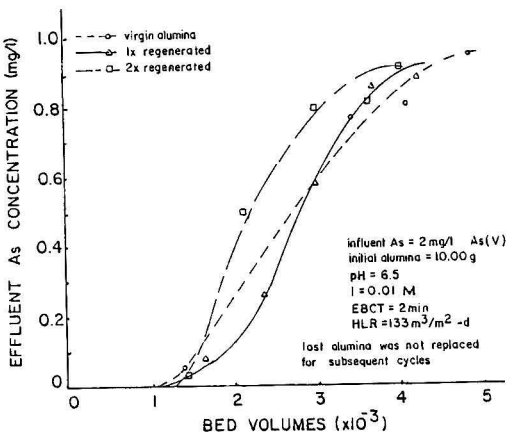


Figure 11. Effect of multiple regenerations on capacity of alumina.

the Industrial Waste Elimination Research Center, Illinois Institute of Technology, Chicago, July 27-August 1, 1986.

#### LITERATURE CITED

1. Irgolic, K. J., "Speciation of Arsenic Compounds in Water Supplies," EPA-600/1-82-010 (1982).
2. Blakely, N. C., "Behavior of Arsenical Wastes Codisposed with Domestic Solid Wastes," *J. Water Poll. Control Fed.*, 56: 56(1), p. 69 (Jan., 1984).
3. Reece, D. E., "Influence of Chemical Species on Subsurface Arsenic Contamination," Paper presented at the Conference of National Well Water Assoc., Houston, TX (July, 1984).
4. Woolson, E. A., "Man's Perturbation of the Arsenic Cycle," in *Arsenic*, W. H. Lederer and R. J. Fensterhelm, Eds., Van Nostrand Reinhold Co., New York (1983).
5. Penrose, W. R., "Arsenic in Marine and Aquatic Environment: Analysis, Occurrence and Significance," *CRC Critical Rev. Environ. Control*, 4, p. 452 (1974).
6. Ferguson, J. F. and J. Gavis, "A Review of the Arsenic Cycle in Natural Waters," *Water Research*, 6(10), p. 1259 (Oct., 1972).
7. Shen, Y. S., "Study of Arsenic Removal from Drinking Water," *J. Amer. Water Wks. Asscn.*, 65(8), p. 543 (Aug., 1973).
8. Gullledge, H. and J. T. O'Connor, "Removal of Arsenic (V) from Water by Adsorption on Aluminum and Ferric Hydroxides," *Jour. Amer. Water Wk. Asscn.*, 65(8), p. 548 (Aug., 1973).
9. Logsdon, G. S. et al., "Removal of Heavy Metals by Conventional Treatment," in *Proc. 16th Water Qual. Conf.*, University of Illinois, Urbana, IL, p. 111-133 (Feb., 13-14, 1974).
10. Lee, J. Y. and R. G. Rosehart, "Arsenic Removal by Sorption Process from Wastewaters," *Canad. Mining Metallurgical Bull.*, 65(11), p. 33 (Nov., 1972).
11. Huang, C. P. and P. L. K. Fu, "Treatment of Arsenic(V)-Containing Water by the Activated Carbon Process," *J. Water Poll. Control Fed.*, 56(3), p. 233 (Mar., 1984).
12. Gupta, S. K. and K. Y. Chen, "Arsenic Removal by Adsorption," *Jour. Water Poll. Control Fed.*, 50(3), p. 493 (Mar., 1978).
13. Rubel, F. and F. S. Williams, "Pilot Study of Fluoride and Arsenic Removal from Potable Water," EPA-600/2-80-100 (Aug., 1980).
14. Rosenblum, E. and D. Clifford, "The Equilibrium Arsenic Capacity of Activated Alumina," EPA-600/S2-83-107 (Feb., 1984).
15. Schlicher, R. J. and M. M. Ghosh, "Removal of Arsenic from Water by Physical-Chemical Treatment," *AIChE Symp. Ser.*, No. 243, Vol. 81, p. 152-164 (1985).
16. Huang, C. P., "The Surface Acidity of Hydrated Solids," in *Adsorption of Inorganics at Solid-Liquid Interfaces*, M. A. Anderson and A. J. Rubin, ed., p. 183-217, Ann Arbor Science Publishers, Inc., Ann Arbor, MI (1981).
17. Hiemenz, P. C., *Principles of Colloid and Surface Chemistry*, Second Edition, Marcel Dekker, Inc., New York (1986). "Hydrated  $\gamma$ - $\text{Al}_2\text{O}_3$ ," *J. Colloid Interface Sci.*, 43, p. 409 (1973).
18. Davis, J. A. and J. O. Leckie, "Surface Ionization and Complexation at the Oxide/Water Interface: III. Adsorption of Anions," *J. Colloid Interface Sci.*, 74, p. 32 (1980).
19. Pierce, M. L. and C. B. Moore, "Adsorption of Arsenite on Amorphous Iron Hydroxides from Dilute Aqueous Solutions," *Env. Sci. Technol.*, 14(2), p. 214 (Feb., 1980).
20. Schindler, P. W., "Surface Complex at Oxide-Water Interfaces," in *Adsorption of Inorganics at Solid-Liquid Interfaces*, M. A. Anderson and A. J. Rubin, eds., p. 1-49, Ann Arbor Science Publishers, Inc., Ann Arbor, MI (1981).
21. Chen, Y. R., J. N. Butler, and W. Stumm, "Adsorption of Phosphate on Alumina and Kaolinite from Dilute Aqueous Solutions," *J. Colloid Interface Sci.*, 43, p. 421 (1973).
22. Hingston, F. J., "A Review of Anion Adsorption," in *Adsorption of Inorganics at Solid-Liquid Interfaces*, M. A. Anderson and A. J. Rubin, eds., p. 51-90, Ann Arbor Science Publishers, Inc., Ann Arbor, MI (1981).
23. Cabrera, F., L. Madrid, and P. DeArambarri, "Adsorption of Phosphate by Various Oxides: Theoretical Treatment of the Adsorption Envelope," *J. Soil Sci.*, 28, p. 305 (1977).
24. Westall, J., "Chemical Equilibrium Including Adsorption on Charged Surfaces," in *Advances in Chemistry Series No. 189*, p. 33-44, Amer. Chem. Soc. (1980).
25. Anderson, M. A. and D. T. Malotky, "The Desorption of Protolyzable Anions on Hydrated Oxides at the Isoelectric pH," *J. Colloid Interface Sci.*, 72, p. 413 (1979).



**Mriganka M. Ghosh**, professor of civil engineering and area leader of the environmental engineering program at the Pennsylvania State University received his Ph.D. in environmental engineering from the University of Illinois. He was the editor of the *Journal of Environmental Engineering*, ASCE and is currently the Vice-Chairman of the Environmental Engineering Division, ASCE. A co-winner of the Academic Achievement Prize of the American Water Works Association in 1981 and 1985, he has authored over 80 technical publications.

**Jill R. Yuan**, is associate professor of environmental engineering at the National Chung Hsing University, Taichung, Taiwan. She received a Ph.D. in environmental engineering from the University of Missouri at Columbia, MO. She has made several presentations at national meetings in the U.S. and at an international meeting in Vienna in March, 1986. She has authored four technical papers in U.S. journals.

# Rapid Renovation of a Sludge Lagoon

E. A. Dienemann, J. F. Magee II, D. S. Kosson and R. C. Ahlert

Rutgers, The State University of New Jersey, Department of Chemical and Biochemical Engineering, P.O. Box 909, Piscataway, NJ 08854

*The application of a soil-based microbial treatment process for renovation of natural leachate and forced extracts from an industrial sludge lagoon has been examined. Laboratory soil column experiments, with influent TOC concentrations up to 2270 mg/l, obtained reductions in dissolved organic carbon that ranged from 90% to 99%.*

*Previous work indicates that these results can be extrapolated to field conditions.*

## INTRODUCTION

Recent revisions of the Resource Conservation and Recovery Act (RCRA) have provided new incentives for the renovation of surface impoundments and landfills. This has stimulated interest in finding safe, economical treatment alternatives for disposal lagoons. On-site treatment technologies are particularly promising because they offer both economic and safety advantages by eliminating the need for major excavation and off-site transportation of hazardous wastes.

For over ten years, the industrial sludges from a chemical manufacturing firm were primarily disposed of in a single surface impoundment. The rate of deposition and the composition of the sludges being deposited varied, resulting in layering within the receiving lagoon. Two of the principal wastes of concern in the lagoon are primary and secondary (biological) sludges from diverse chemical manufacturing. At some time during the operation of the lagoon, large quantities of lime were applied to the surface in order to suppress odors. However, the extent of the lime application and, therefore, the quantity present in the sludges, is unknown. The sludges, which are solid, produce a leachate that affects local groundwater.

Renovation of the lagoon involves two interrelated problems. The first is the removal of organic and inorganic contaminants from the solid matrix in the lagoon, without major excavation. The second is the treatment of removed contaminants in the resulting waste stream. Preliminary studies indicate that *in-situ* extraction of the sludges is possible [1]. Furthermore, representative samples of sludge that were extracted with dilute aqueous sodium hydroxide, suggest that exhaustive leaching can take place.

Two methods for the treatment of natural leachate and forced extracts were considered for implementation. The first method involved conventional aerobic biodegradation, employing acclimated cultures obtained from the secondary sludge of a municipal sewage treatment facility [2]. Reductions in dissolved total organic carbon (TOC) of up to 50% were possible using this system.

The second method, which is the subject of this paper, was a soil based microbial treatment system. In this pro-

cess a mixed microbial population is developed in the soil structure; the leachate or extract to be treated is applied to the soil surface so that it will percolate through the soil column. During this process aerobic degradation occurs near the surface, where oxygen is available from atmospheric diffusion, and is followed by anaerobic degradation, which dominates at greater depths. Process control is maintained through management of influent loading rates and concentrations. This paper will examine the development and application of this process to a sludge lagoon case study; for additional background on the development of the process, see Kosson and Ahlert [3].

## MATERIALS AND METHODS

Samples of natural leachate (Table 1) were obtained from the lagoon at the study site. Samples of both primary and secondary sludges were excavated from the lagoon (Table 2).

The extract for use in the experiments was obtained by agitating the appropriate quantity of sludge, in contact with 0.005N aqueous sodium hydroxide (pH 11.5), for 48 hours. Two liters of extractant per kilogram of sludge were used. After the resulting mixture was allowed to settle, the decanted supernatant was centrifuged and recarbonated with pure CO<sub>2</sub> until a pH of 7.0 was obtained. The recarbonated liquid was filtered to remove any floc. The extracts from the primary and secondary sludges were mixed in proportions similar to those found in the actual sludge disposal lagoon. The characteristics of the resulting extract are presented in Table 3.

The laboratory soil column experiments were designed to investigate the ability of mixed microbial populations in a soil structure to biodegrade the natural leachate and forced extracts. Previous experiments have shown that data obtained from laboratory scale investigations are readily extrapolated to field situations [3, 4]. Hydraulic conductivity (permeability), hydraulic loading, organic loading, buffering and pH, and soil adsorption, which are all important, interrelated variables, were taken into consideration during the study. In order to obtain as much data as possible from a limited number of columns, frac-

TABLE 1. LEACHATE CHARACTERISTICS

pH	6.5-7.7
TOC (mg/l)	170-5000
NH <sub>3</sub> (mg N/l)	11-620
TKN (mg N/l)	25-820
NO <sub>3</sub> <sup>-</sup> (mg/l)	<0.01
Total P (mg/l)	<1.5
Cl <sup>-</sup> (mg/l)	<20
Residue (103°C, 24 hr)(mg/l)	2750-4280
TDS (mg/l)	2610-4080
Metallic Species (mg/l)	
Ag	.11 - .011
Al	1.1 - .11
B	.011- .0011
Ba	.11 - .011
Ca	11.0 -110.0
Cr	.011- .0011
Cu	.11 - .011
Fe	11.0 - 1.1
Mg	11.0 - 11.0
Mn	11.0 - 1.1
Na	110.0 - 11.0
Ni	.11 - .011
Pb	.11 - .011
Si	11.0 - 1.1
Sn	.011- .0011
Ti	.11 - .011
Zn	1.1 - .11

tional factorial designs were employed. The following three parameters were the primary factors considered: column packing, organic loading, and inhibition of microbial activity.

The first parameter, column packing, was considered because of its influence, via adsorption, on solute retention, reduction and removal; packing also controls hydraulic conductivity and porosity. To examine these effects two column packings were chosen. The first column packing was a sandy loam, which was selected based on previous experience with a similar soil and because of its availability on site. The characteristics of the sandy loam used are presented in Table 4. The second column packing was comprised of the same sandy loam with activated

TABLE 3. EXTRACT CHARACTERISTICS

	Primary Extract	Secondary Extract	Combined Extract
pH	7.0	7.0	7.0
TOC (mg/l)	400	2500	2080
NH <sub>3</sub> (mg/l)	91	400	338.2
TKN (mg/l)	235	640	559
TDS (g/l)	1.3	6.8	5.7
VFA as TOC (mg/l)			
Acetic	<25	772	617.6
Propionic	<25	283	226.4
Isobutyric	<25	158	126.4
Butyric	<25	267	213.6
Total	<25	1480	1184
Na <sup>+</sup> (mg/l)	241	261	257
Ca <sup>++</sup> (mg/l)	89	906	742.6

carbon (Calgon PCB 30 × 140) added. The particle size distribution of this activated carbon is in the sand range, and results in increased packing permeability and adsorptive capacity.

The second parameter that was varied was organic carbon loading, which is influential in the rate of bioslime growth. It has been shown that the rate of bioslime growth may be directly or inversely proportional to influent TOC, depending on the composition of the influent [5]. Therefore, two influent concentrations, nominally full-strength or half-strength leachate or extract, were considered in each experiment.

The third parameter examined was the effect of high concentrations of chloride ion and/or sodium azide on the inhibition of microbial activity. This aspect was carried out to determine if representative "sterile" control columns could be maintained. Results were anticipated to yield information on retardation of bioslime development and to verify sorptive contributions to process operation.

Each laboratory column (LC) consisted of 7.6 cm diameter glass process pipe, with an effective packing depth of 46 cm. The foundation of the packing consisted of 2.5 cm of sand, a thin (0.3 cm) layer of glass wool and 5 cm of glass beads. The columns were operated with 100 mm Hg of vacuum applied continuously at the base, through the collection flasks. The vacuum balanced the capillary forces acting in the soil structure, in an effort to replicate field conditions. This apparatus configuration was suitable because of the absence of volatile organic species in the aqueous stream to be treated. The outside of each column was covered to prevent photosynthesis.

Each LC received 30 ml inoculum of a mixed microbial population acclimated from the secondary sludge of a municipal sewage treatment plant. Acclimation procedures are described by Boyer, *et al.* [2].

#### TREATMENT OF NATURAL LEACHATE

Sixteen laboratory soil columns were operated to examine treatment of naturally occurring leachate. Full-strength and half-strength leachate was employed as

TABLE 2. PRIMARY AND SECONDARY SLUDGE CHARACTERISTICS

Characteristic	Primary Sludge	Secondary Sludge
Apparent Density (g/cm <sup>3</sup> )	1.16	1.12
%Solids (103°C, 24 hr)	28.0	23.0
%Solids (550°C, 12 hr)	22.4	15.6
Total C (% on a dry wt basis)	7.2	16.3
Inorganic Species (% on a dry wt basis)		
Al	10-100	1-10
B	.001-.01	—
Ba	.1-1.	.001-.01
Ca	10-100	10-100
Cr	.1-1	.01-.1
Cu	.01-1	.01-.1
Fe	1-10	1-10
Mg	.1-1	.1-1
Mn	.01-.1	.01-.1
Na	.1-1	.1-1
Ni	.001-.01	.001-.01
P	.1-1	.1-1
Pb	.01-.1	.01-.1
Si	10-100	1-10
Sn	—	.001-.01
Ti	.1-1	.01-.1
V	.001-.01	.001-.01

TABLE 4. SOIL PROPERTIES

pH	Mg (mg/kg)	P (mg/kg)	K (mg/kg)	Ca (mg/kg)	Organic Carbon %
5.2	92	228	56	581	0.84
Cation Exchange Capacity: 5.68 MEQ/100g					
Mechanical Analysis					
Sand: 68%					
Silt: 20%					
Clay: 12%					
Texture: Sandy Loam					

influent for both packing types. Packings containing sandy loam mixed with activated carbon contained 10 wt % activated carbon. In addition, full-strength leachate was supplemented with either chloride or sodium azide and chloride to study inhibition of microbial growth. Two replications were performed for each trial case. LCs receiving influent without inhibitors were operated continuously for 100 days. LCs receiving influent containing inhibitors were operated continuously for 50 days.

#### Operating Summary and Visual Observations

Effluent appearance was an important indicator of conditions in a column. Effluent appearance varied widely throughout the experiment, and was a strong function of column packing and influent salt composition. Columns packed with the soil-GAC mixture (LCs 1, 2, 3, 4, 5A and 12A) produced a brown, turbid effluent. This was a direct result of fine silt and clay particles "washing out" of these columns. This phenomenon was not affected by subsequent establishment of microbial colonies or addition of leachate. Wash-out did seem to be aggravated, however, by addition of the sodium chloride inhibitor to LCs 5A and 12A. This clay particle wash-out was not observed for any of the columns packed with sandy loam, only (LCs 6, 7, 8, 9, 10A and 11A). Effluent from these columns was generally free of turbidity for the duration of the experiment. However, all of these columns exhibited substantially lower hydraulic fluxes compared to columns packed with the soil-carbon mixture.

These contrasting observations were thought to be the result of disaggregation of the soil's clay fraction in response to a cationic imbalance in the feed solutions. The resulting dispersed clay particles either, i) passed through the larger interparticle pores present in columns packed with the soil-carbon mixture, washing-out with the effluent, or ii) became trapped in the smaller interparticle pores present in columns packed with soil only, contributing to column plugging.

It has been shown that the state of aggregation of the clay fraction in a soil is greatly affected by the absolute amount and relative ratio of monovalent and divalent cationic species [6, 7, 8]. If the influent sodium adsorption ratio (SAR), i.e.,

$$\text{SAR} = (\text{Na}^+)/2[(\text{Ca}^{++}) + (\text{Mg}^{++})]^{1/2}, \text{ where } ( ) = \text{millimoles/l}$$

is too high or the level of divalent cations is too low, elevated levels of monovalent cations, relative to divalent cations, will exist in the soil water and be adsorbed reversibly at the soil surface. Monovalent cations, especially  $\text{Na}^+$ , are loosely held compared to divalent cations like  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$ , and do not effectively reduce the natural electronegativity of clay micelles. This leads to electrostatic repulsion between individual micelles, resulting in dispersion of the once-large aggregate of clay micelles. Reintroduction of appropriate levels of divalent cations can reverse this condition, allowing the dispersed micelles to reaggregate. The literature [6, 7] advises that the influent SAR should be less than 12 to avoid disaggregation in a sandy loam. In addition, a minimum divalent cation level of 0.01M has been suggested to avoid disaggregation [6, 7].

Anderson, *et al.* reported that once disaggregation occurs, migration of the dispersed clay particles through a soil matrix with relatively large interparticle pores can occur [9]. Other researchers have reported disaggregation followed by clogging of the interparticle pores, restricting flow [6, 7]. The size of interparticle pores determines which phenomenon is observed.

To test this clay disaggregation/migration-relative-to-pore-size hypothesis, the influent SAR and divalent cat-

ion level was controlled independently. It was not desired to test the effects of influent salt composition on the microbially active, uninhibited columns; unwanted inhibitory effects may have resulted. Leachate was the principal source of cations in the influents to the uninhibited columns, with Na, Ca and Mg, each at less than 0.005M. This information supported the hypothesis that influent salt composition caused disaggregation (low divalent cation level).

Influent salt composition was varied for the inhibited columns; additional inhibition due to this was not undesired. On Day 23 calcium chloride was substituted for sodium chloride, such that influent SAR was less than 12 and the divalent cation concentration ( $\text{Ca}^{++}$ ) was greater than 0.005M. LC 12A exhibited a dramatic reversal of clay particle wash-out; by Day 43, column effluent was colorless and free of turbidity. This occurred after approximately 1.5 mean residence times. LC 5A showed no sign of reversal through the end of operation (Day 49). This was probably due to severe channeling through the column packing, which did not allow sufficient contact between the cationically balanced influent and the soil matrix. No cessation of clay particle wash-out was observed for similarly packed, uninhibited columns with unadjusted influent salt composition.

As the experiment progressed, development of microbial colonies throughout the column packing became apparent. Distinct regions in the columns became dark-grey to black in color, especially near the surface. Further evidence of microbial growth was the appearance of tiny holes at the packing surface. These holes were probably the result of escaping gases produced by microbial respiration and fermentation. These phenomena were observed in all of the columns, including those that were being examined for microbial inhibition. In fact, through the first 49 days of the experiment, effluent TOC concentrations from the inhibited columns in Part A were not significantly higher than those from the uninhibited counterparts. This was true for each packing type. It was

TABLE 5. LABORATORY SOIL COLUMN RESULTS—LEACHATE INFLUENT

Column	6, 8	7, 9	1, 3	2, 4
Packing Type	Soil	Soil	Soil+GAC	Soil+GAC
Leachate Feed	Full	Half	Full	Half
Influent TOC (mg/l)	750	375	750	375
Average Hydraulic Flux (l/m <sup>2</sup> /day)	3.8, 7.8	7.7, 12	28, 28	28, 30
Average TOC Reduction (g/m <sup>2</sup> /day)	3.4, 6.7	3.4, 6.0	21, 22	11, 13
Overall TOC Removed (% mass basis)	97, 97	98, 93	92, 94	94, 94
Column	10, 11	5, 12	10a, 11a	5a, 12a
Packing Type	Soil	Soil+GAC	Soil	Soil+GAC
Leachate Feed	Full+Cl	Full+Cl	Full+Cl + NaN <sub>3</sub>	Full+Cl + NaN <sub>3</sub>
Influent TOC (mg/l)	750	750	750	750
Average Hydraulic Flux (l/m <sup>2</sup> /day)	20, 13	28, 29	23, 25	25, 27
Average TOC Reduction (g/m <sup>2</sup> /day)	18, 12	23, 26	11, 14	17, 19
Overall TOC Removed (% mass basis)	88, 97	96, 95	64, 74	91, 93

concluded that addition of chloride ion at 1000 mg/l had a limited, if any, inhibitory effect on microbial activity. It was decided to discard the column packings, repack the columns as before, and investigate the possibility of maintaining a totally sterile laboratory column. This became Part B of the microbial inhibition study.

After repacking, four columns were operated for several days with a distilled water influent to estimate column permeability. Before addition of leachate to these columns commenced (Day 1), they were "dosed" for three days with a cationically balanced (SAR less than 12) 0.05 wt% sodium azide solution to inhibit the indigenous microflora. These columns were not inoculated with an active microbial population. Subsequent leachate-containing feed solutions contained at least 0.05 wt% sodium azide inhibitor by weight, and were cationically balanced by addition of calcium salts. By Day 10 (approximately 1.5 mean residence times), effluent from LCs 5B and 12B became transparent and colorless and remained that way until the end of the experiment (Day 51).

These four columns also exhibited visible signs of biological growth, including the establishment of dark-colored regions, and the presence of tiny holes at the column's surface. This occurred despite the presence of a severe inhibitor, and despite the absence of a microbial inoculum or supplemental nutrients, such as potassium and phosphorus.

#### Volumetric Flux Responses

Average hydraulic flux data for each column are presented in Table 5. For the uninhibited columns, the volumetric flux through the columns packed with the soil-carbon mixture was generally three to four times that of

the columns packed with soil only. Within packing types, hydraulic responses were independent of organic (TOC) loading rates. Typical hydraulic flux rates were 28 l/m<sup>2</sup>/day for the mixed soil-carbon packing, and 8 l/m<sup>2</sup>/day for the soil only packing.

For the columns in Part A of the microbial inhibition study, the volumetric flux through the columns packed with the soil-carbon mixture was generally twice that of the columns packed with soil only. Once again, typical hydraulic flux rates were 28 l/m<sup>2</sup>/day for the mixed soil-carbon packing. However, hydraulic flux rates were between 14 and 19 l/m<sup>2</sup>/day for columns packed with soil only, roughly a two-fold increase over the similarly packed, uninhibited columns.

For the columns in Part B of the microbial inhibition study, there was only a small difference in hydraulic flux rates between the two column packings. As before, hydraulic flux rates were near 28 l/m<sup>2</sup>/day for the mixed soil-carbon packing. However, hydraulic flux rates increased to near 25 l/m<sup>2</sup>/day for the columns packed with soil only, most likely the result of increased microbial inhibition and balanced cationic species.

#### Total Organic Carbon Responses and Reductions

Initially, for each column, effluent TOC concentrations remained close to effluent TOC concentrations obtained from a distilled water feed. Subsequently, for the uninhibited columns, and for the inhibited columns from Part A, there was a noticeable increase in effluent TOC, followed by establishment of a relatively steady state effluent TOC concentration (Figure 1). For the columns in Part B of the microbial inhibition study, the increase in

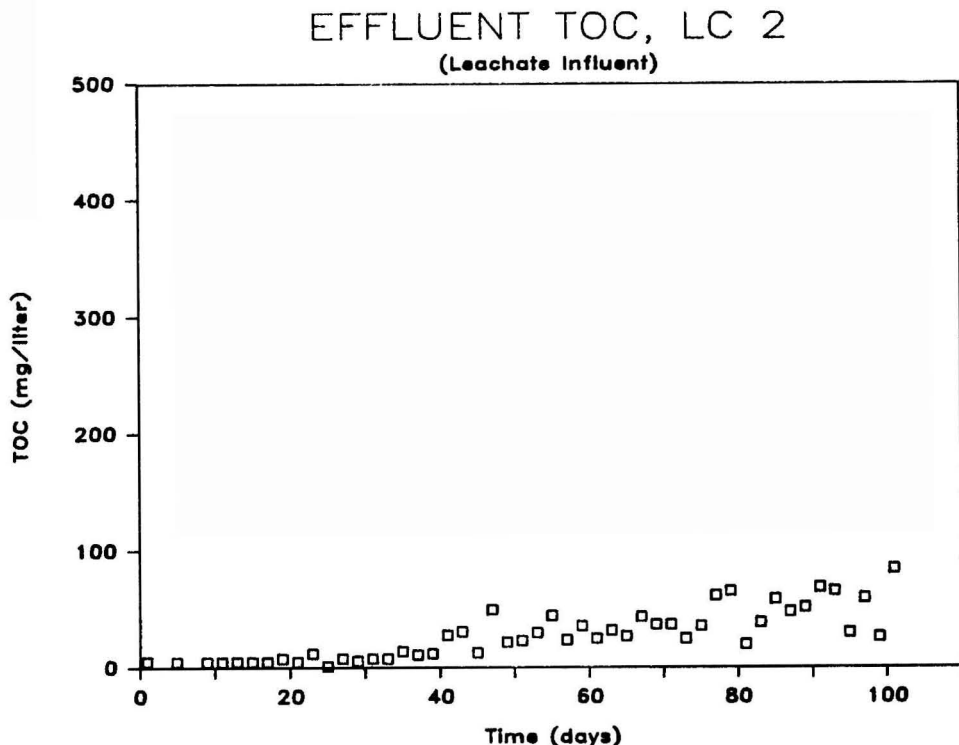


Figure 1

effluent TOC was more pronounced and was followed by a decrease before a relatively steady-state effluent TOC concentration was established. Similar effluent TOC concentration responses had been observed in previous experiments with other leachates [3, 4, 5].

Effluent TOC concentration responses are indicative of the physical, chemical and biological status of a column. These responses are the result of three major competing processes: convective plug flow with dispersion, adsorption and biodegradation. A numerical model incorporating these processes has been developed to simulate experimental responses of active microbial reactor columns [10]. During operation, one or more of these processes may control, during different time intervals. In general, column responses can be separated into three regimes.

The first regime, during which effluent TOC concentrations remain near zero is a characteristic response delay. Microbial populations are small and adsorption and dispersion are the primary TOC reduction processes. The duration of this response delay is dependent on TOC loading, hydraulic flux and the adsorptive capacity of the column packing. Within each packing type, the response delay was approximately half as long for columns fed full-strength leachate as compared to columns fed half-strength leachate, with similar hydraulic fluxes.

During the second regime effluent TOC concentrations either rise to a relatively steady-state level or rise to a peak and decline to a steady-state level. This regime is observed after the adsorptive capacity of the column packing has been exhausted. The rise in effluent TOC concentration is characteristically accompanied by a rise in effluent pH. The absence or presence of the peak depends on the ability of the microbial community to adapt

to the increase in available organic carbon. A peak was only observed for the columns in Part B of the microbial inhibition study. This probably resulted from sodium azide inhibition and the absence of an initial microbial inoculum. The third regime is demonstrated by attainment of a relatively constant effluent TOC concentration level. This response results from the microbial community becoming fully developed and adapted to the increase in available organic carbon; a pseudo-steady-state is reached. Sufficient microflora are present to degrade most, if not all, available substrate. Columns fed full-strength leachate generally established steady-state effluent TOC concentrations twice that of columns fed half-strength leachate. No clear relationship between effluent TOC concentration and packing type was observed. On an integrated mass basis, LCs fed full-strength leachate removed approximately twice as much TOC as those fed half-strength leachate, with the same packing. In addition, uninhibited LCs packed with soil supplemented with activated carbon removed approximately three times as much TOC as those packed with soil, only. This effect was primarily a reflection of differences in hydraulic flux. Typical values for TOC reductions are presented in Table 5.

For the columns from Part B, the added effect of microbial inhibition on mass of organic carbon removed was evident, especially for the columns packed with soil only. Even though the soil-only packed columns from Part B had significantly higher fluxes than counterparts from Part A, a lower average mass of TOC was removed per day. This relationship was observed, but was much less pronounced, for columns packed with the soil-carbon mixture.

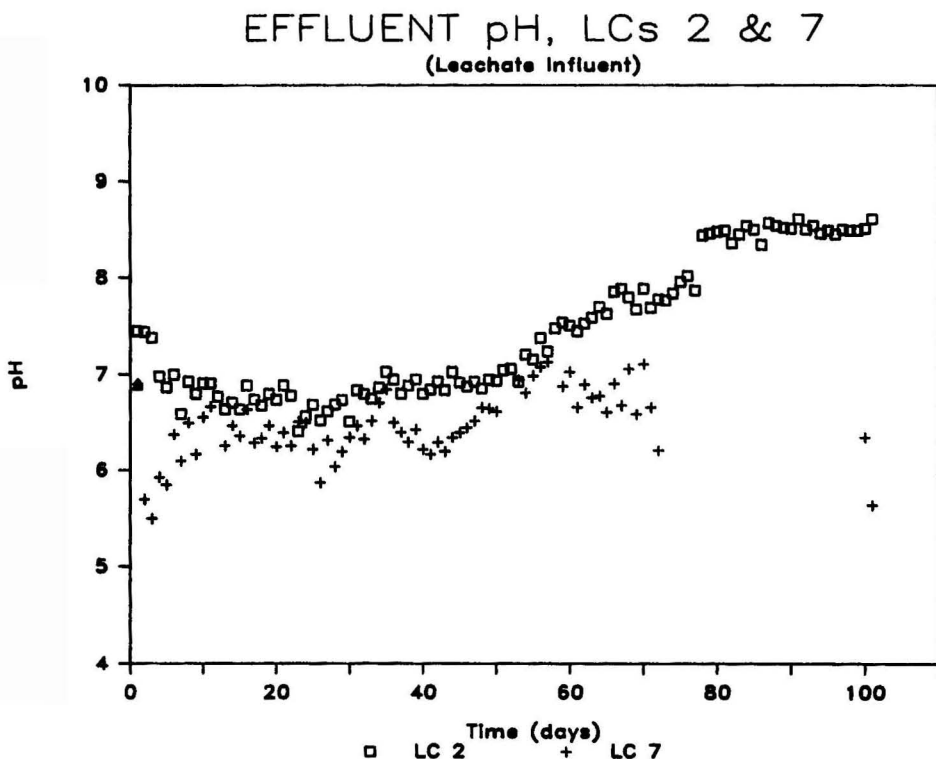


Figure 2



TABLE 6. LABORATORY SOIL COLUMN RESULTS—  
EXTRACT INFLUENT

Column	1, 2	3, 4	5, 6	7, 8
Packing Type	Soil+ GAC	Soil+ GAC	Soil+ GAC	Soil+ GAC
Leachate Feed	Half	Full	Full+ NaN <sub>3</sub>	Cl <sup>-</sup> only +Ca
Influent TOC (mg/l)	1135	2270	2270	—
Average Hydraulic Flux (l/m <sup>2</sup> /day)	33, 36	34, 40	50, 49	50, 50
Average TOC Reduction (g/m <sup>2</sup> /day)	37, 40	76, 89	81, 81	—
Overall TOC Re- moved (% mass ba- sis)	99, 99	99, 99	71, 72	—

#### Effluent pH

Columns that experienced decreasing hydraulic flux exhibited an acidic effluent pH throughout operation, while columns which maintained a relatively constant hydraulic flux exhibited effluent pH responses corresponding to the effluent TOC response regimes (Figure 2). For the latter case, the initial neutral effluent corresponds to the first effluent TOC regime, which is a reflection of packed bed mean residence time. During this period, the effluent pH is indicative of the natural soil-water pH. The rise in effluent pH occurs soon after the second effluent TOC regime, in which effluent TOC concentrations rise.

Finally, effluent TOC concentration and effluent pH reach relatively constant levels. These results are a function of the status of microbial community and the influent composition. Effluent pH responses reflect creation and destruction of volatile fatty acids (VFAs). High influent VFA concentrations in conjunction with acetogenesis results in decreased effluent pH, while methanogenesis accompanied with complete destruction of VFAs results in elevated effluent pH. Similar effluent pH relationships have been observed in previous experiments [5].

#### TREATMENT OF SLUDGE EXTRACT

To examine the treatment of sludge extract, four trial cases, each of which was replicated, were investigated. All of the LCs were packed with sandy loam mixed with 5% activated carbon, by weight. Full-strength and half-strength extract and full-strength extract augmented with sodium azide were employed as influent. Calcium nitrate was added, as needed, to all influents to maintain the influent SAR at less than 1.4. In addition, two LCs were operated with an influent containing chloride and no extract, to estimate the hydraulic characteristics of the packing. Effluent chloride concentration was monitored to develop a residence time distribution. Estimates of the packed bed porosity and dispersion coefficient were 0.30 and 6.0 cm<sup>2</sup>/day, respectively.

Column responses were generally similar to those observed with columns operated with natural leachate. The LCs receiving full-strength and half-strength extract as influent experienced plugging at regular intervals throughout the experiment, although this was easily remedied by regularly repacking the top 1 in. of the col-

EFFLUENT TOC, LCs 2 & 3  
(Extract Influent)

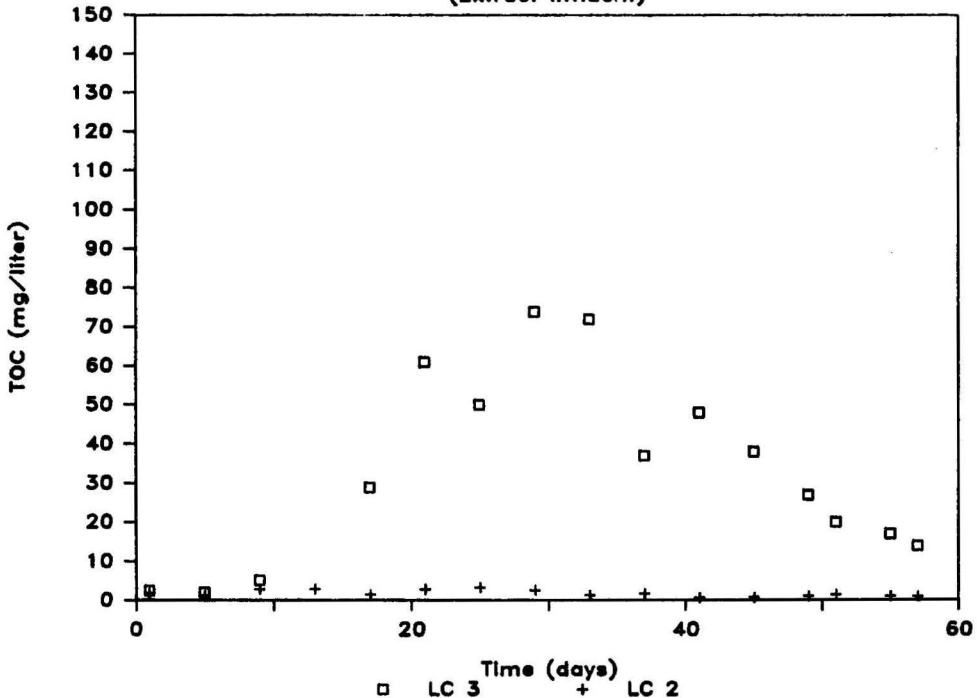


Figure 3

## EFFLUENT TOC, LC 6 (Extract with Azide Influent)

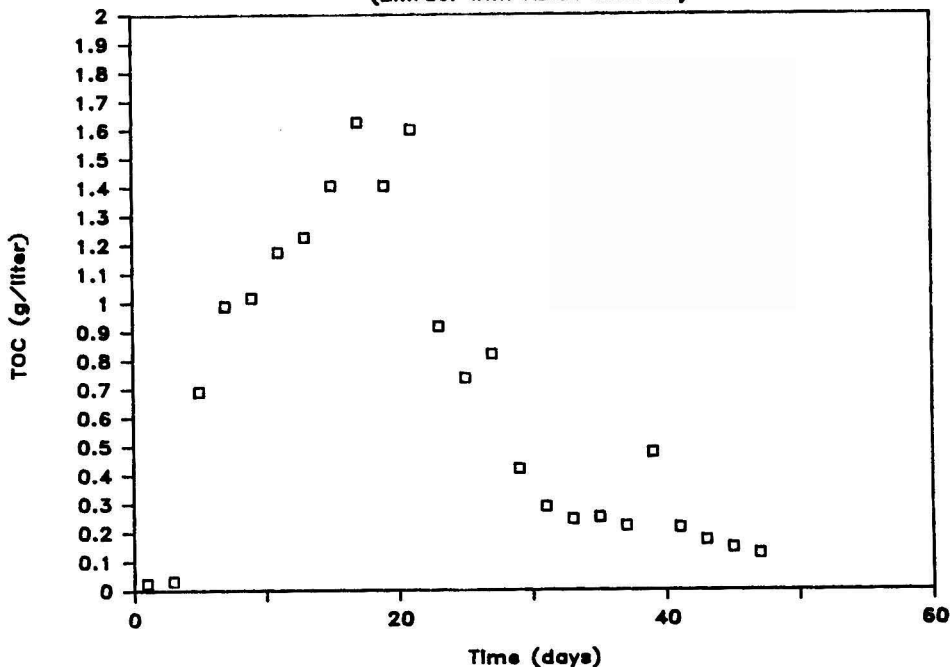


Figure 4

umn. Hydraulic flux was augmented further by maintaining the influent SAR at less than 1.4 (Table 6). No turbidity was observed in the effluent.

The columns that were fed full-strength extract demonstrated TOC reductions in excess of 97%, while the columns fed half-strength extract demonstrated TOC reductions in excess of 99%, throughout the duration of the experiment (Table 6, Figure 3). On a mass basis, the columns fed full-strength extract removed approximately twice as much TOC as columns fed half-strength extract.

The effluent pH, for LCs that were fed half-strength extract, decreased rapidly from an initial neutral level to an acidic pH of approximately 4. The pH levels, which subsequently fluctuated between 4 and 5, paralleled the variation in the hydraulic flux. LCs fed full-strength extract followed the pattern for properly functioning columns.

In an attempt to decrease microbial activity in a trial case where no inoculum was used, increased amounts of sodium azide were added to the full-strength extract. The concentration of sodium azide in the influent, for the inhibition trial case, was 1.0%, by weight. The inhibitory effects observed in this situation were greater than those observed during the experiments with leachate. A typical effluent TOC response is presented in Figure 4.

### CONCLUSIONS

Soil-based microbial treatment is a viable process for renovation of natural leachate and forced extracts from an industrial sludge lagoon. The reductions obtained in dissolved organic carbon ranged between 90% and 99%, depending on the packing type, the additives in the leachate feed, and the rate of influent feed. Previous work indicates that these results can be extrapolated to field conditions.

Hydraulic flux seems to be the limiting factor determining treatment capacity, i.e., the rate and total mass of organic carbon that can be mineralized. As hydraulic flux increased, the mass of organic carbon removed increased, at each influent TOC level. Hydraulic flux is strongly influenced by column packing, influent salt composition and microbial growth rate. An imbalance in influent salt composition leads to disaggregation of clay structure. This was followed by clay particle wash-out in the columns packed with a soil-carbon mixture, due to the larger interparticle pores present. For the columns packed with soil-only this led to plugging of the smaller interparticle pores, and resulted in decreased hydraulic flux. Plugging can be aggravated by rapid microbial growth. These effects (wash-out and plugging) can be reversed or prevented, to some extent by balancing influent cationic species. Microbial inhibition can mitigate column plugging, also. However, the percentage of organic carbon removed may be diminished. These effects were much more pronounced for sodium azide inhibition than for chloride inhibition.

Effluent TOC concentration responses are indicative of column status. Every column exhibited an initial response delay, during which adsorption was the primary TOC removal process. This was followed by a rise in effluent TOC concentration after the adsorptive capacity of the column packing was exhausted. Subsequently, a relatively steady-state effluent TOC concentration was established, corresponding to microbial adaptation to the leachate. A peak was observed before this steady-state was established, for the columns to which sodium azide was added. This is indicative of a significant degree of microbial inhibition due to the sodium azide. However, it is important to note that without inoculation, and under se-

vere inhibitory conditions, the indigenous microflora still developed sufficiently to degrade most of the organic carbon in the leachate or extract.

#### LITERATURE CITED

1. Kosson, D. S., R. C. Ahlert, J. D. Boyer, E. A. Dienemann, and J. F. Magee II, "Development and Application of On-site Technologies for Sludge Filled Lagoons," *Proceedings: International Conference on New Frontiers for Hazardous Waste Management*, EPA/600/9-85/025, 118-127 (1985).
2. Boyer, J. D., M. B. King, D. S. Kosson, and R. C. Ahlert, "Aerobic Biodegradation of Leachate and Forced Extracts from a Sludge Disposal Lagoon," *Toxic and Hazardous Wastes*, Technomic Publishing Co., Lancaster, PA, 497-508 (1985).
3. Kosson, D. S. and R. C. Ahlert, "In-situ and On-site Biodegradation of Industrial Landfill Leachate," *Environmental Progress*, 3, 176-183 (August 1984).
4. Kosson, D. S., E. A. Dienemann, and R. C. Ahlert, "Characterization and Treatability Studies on Industrial Landfill Leachate (Kin-Buc I)," *Proc. 39th Annual Purdue Industrial Waste Conference*, W. Lafayette, IN (May 1984).
5. Kosson, D. S., E. A. Dienemann, and R. C. Ahlert, "Treatment of Hazardous Landfill Leachates Utilizing In-situ Microbial Degradation, Part II," *Proc. Hazardous Wastes and Environmental Emergencies*, HMCRI, Houston, TX, 289-292 (March 1984).
6. Overcash, M. R. and D. Pal, *Design of Land Treatment Systems for Industrial Wastes-Theory and Practice*, Ann Arbor Science Publishers Inc., Ann Arbor, MI (1979).
7. Hillel, D., *Introduction to Soil Physics*, Academic Press, New York (1982).
8. Brady, N. C., *The Nature and Properties of Soils*, 8th Ed., Macmillan Publishing Co., Inc., New York (1974).
9. Anderson, D. C. and S. G. Jones, "Clay Barrier — Leachate Interaction," *Proc. Management of Uncontrolled Hazardous Waste Sites*, HMCRI, Washington, D.C., pp. 154-160 (1983).
10. Kosson, D. S., G. C. Aguihotri, and R. C. Ahlert, "Modeling and Simulation of a Soil-Based Microbial Treatment Process," *J. of Hazardous Materials*, In Press.

**Erik A. Dienemann** is an interdisciplinary doctoral student in the fields of chemical engineering and environmental policy at Rutgers University. His current focus is technical and regulatory considerations for the application of in-situ and on-site treatment technology at Superfund sites.

**John F. Magee II** is a doctoral student in chemical engineering at Rutgers University. His principal research interests are the application of separation processes to environmental problems.

**David S. Kosson** is Assistant Professor in the Department of Chemical and Biochemical Engineering at Rutgers University. He earned the Ph.D. in Chemical and Biochemical Engineering from Rutgers University. His primary field of research is the development and application of in-situ and on-site treatment processes for hazardous wastes and groundwater contamination.

**Robert C. Ahlert** is Distinguished Professor of Chemical and Biochemical Engineering at Rutgers University. He earned the Ph.D. in Chemical Engineering from Lehigh University. He spent ten years in industry working in the fields of combustion, applied thermodynamics and catalysis. At the University, his teaching and research interests include hazardous waste management and resource recovery.

# Feasibility of Intermittent Biological Treatment for Hazardous Wastes

A. Scott Weber and Mark R. Matsumoto

Department of Civil Engineering, State University of New York at Buffalo

*During an investigation and evaluation of a former hazardous waste facility, groundwater underlying the site was found to be highly contaminated by a variety of hazardous organic substances. An intermittently operated biological treatment process coupled with activated carbon adsorption was identified as a promising on-site alternative. Because the operating constraints and degree of treatment achieved by biological processes subjected to very infrequent operation were unknown, a pilot study was initiated to assess the technical feasibility of the proposed process. Based on the findings of the experimental study, intermittent biological treatment can achieve significant removal of waste pollutants. The rate of COD removal was found to be adversely affected by decreases in operation frequency and decreased operating temperatures. However, all biodegradable COD was removed within a react period of 24 hrs., despite lag periods as long as three weeks between operation. Addition of powdered activated carbon was tested under one operating scenario and is hypothesized to be advantageous in reducing aeration times for conditions of low temperature and extended lag periods.*

## INTRODUCTION

During a site investigation and evaluation of a former hazardous waste facility in New York, groundwater underlying the site and leachate from the site were found to be highly contaminated by a wide variety of hazardous organic substances. Characteristics of the combined groundwater/leachate are presented in Table I. The recommended remedial plan for site cleanup includes the construction of a leachate system, installation of a groundwater recovery system, and the construction of an on-site treatment facility [1].

Due to the projected low groundwater pumping rates and leachate collection volumes expected during remediation, it is expected that on-site treatment would be most cost effective if carried out on an intermittent basis (i.e. once per week or longer). To determine the treatability of the contaminated groundwater and leachate collected from the site, a preliminary study was conducted by the Department of Civil Engineering at the State University of New York at Buffalo. Based on the findings of the preliminary analyses, a coupled biotreatment/activated carbon system was identified as the most promising on-site treatment alternative [2].

As originally planned, the proposed onsite system was to consist of a batch biological reactor followed by granular activated carbon columns for removal of non-biodegradable organics. The potential of using batch biological treatment processes, commonly referred to as sequencing

batch reactors (SBR), for waste treatment has been demonstrated previously by Irvine and coworkers [3-5]. However, in the studies conducted by Irvine, the time between operation cycles, or the idle time, was relatively short; typically less than one day. Because the operating constraints and degree of treatment achieved by biological processes subjected to very infrequent operation are unknown, a pilot study was initiated to assess the technical feasibility of the proposed process.

## DESCRIPTION OF THE SBR SYSTEM

The sequencing batch reactor (SBR), a type of periodic process, is a fill and draw activated sludge system. The operation cycle of a typical SBR is divided into five discrete periods: fill, react, settle, draw, and idle. A brief description of the SBR cycle is presented below. Complete details of SBR operation and performance may be found in references [3, 4, 5].

During the fill period, wastewater is added to the biomass remaining in the tank from the previous cycle. The fill period ends either when the tank is full or when a maximum time for the fill period is reached. The fill period may be conducted with or without aeration.

Following the fill period, the react period is initiated. Reactor contents are mixed and aerated. The total time needed during the react period to achieve optimum organic removal will vary depending on the waste characteristics and the rate of biological degradation.

During settling, solids and liquid are separated. The time for settling should be long enough to ensure that the

Correspondence should be addressed to A. Scott Weber

TABLE 1. POLLUTANTS IDENTIFIED FROM GC/MS SCAN AND CHEMICAL ANALYSES OF GROUNDWATER/LEACHATE

Pollutant identified above detectable limit	Concentration, ug/L
<b>Positively Identified</b>	
Methylene chloride	11,000
Acetone	42,000
trans-1,2-dichloroethane	3,500
2-Butanone	14,000
Benzene	1,500
4-Methyl-2-Pentanone	12,000
Toluene	4,300
Total Xylenes	1,600
Phenol	5,700
Aniline	5,600
2-Methylphenol	2,300
4-Methylphenol	15,000
2,4-Dimethylphenol	3,400
Iron	96,000
Nickel	2,600
COD, mg/L	1,950
TOC, mg/L	1,020
BOD <sub>5</sub> , mg/L	1,090
<b>Tentatively Identified</b>	
Ethyl benzene	620
Oxirane,2,3-Diethyl	28,000
2-Pentanol,4-Methyl	6,400
Benzene, Methyl	8,500
Formamide,N-N-Dimethyl	5,400
Butanoic acid	14,000
Ethanol,1-Methoxy-,Acetate	2,900
Benzene, ethyl-	940
Benzene,1,4-Dimethyl-	2,400
Pentanoic acid	6,300
Butanoic acid, 2-Ethyl-	2,300
2-Pyrrolidinone,1-Methyl	7,900
Benzenamine,N,N-Dimethyl	4,700
Hexanoic acid,2-Ethyl	4,200
Phenol,2,3-Dimethyl	20,000
Benzene acetic acid	1,700
Benzoic acid,3-Methyl-	5,200

sludge blanket remains below the withdrawal mechanism during the draw period, but minimized to prevent rising sludge caused by gas formation during anoxic conditions.

During the draw period, the treated wastewater is removed by decanting. Following this, the system may be placed in an idle period until the next fill period begins. Sludge may be withdrawn during the idle period.

#### EXPERIMENTAL APPROACH

As previously noted, treatment operations at the former hazardous waste site are likely to be required only on an intermittent basis because of expected low site groundwater and leachate collection rates. Periods between operation may be greater than one week. The effects of periodic operation on biological treatment process performance are unknown. To determine the effects of the extended idle periods on organic carbon removal rates and treatment efficiency, experimental studies were conducted. The bioreactors used in these experiments were operated on the following schedules: 1) one reaction cycle per week, or an idle period of six days; 2) one reaction cycle per two weeks, or an idle period of 13 days, and 3) one reaction cycle per three weeks, or an idle period of 20 days.

The site is located in upstate New York, and as such, onsite treatment facilities may be required to operate under cooler temperatures. To investigate the effects of temperature on intermittent biological treatment operations,

study bioreactors were operated under temperatures of 5, 15, and 25°C, using a once per week operating protocol.

As noted in the results section, significant degradation of performance was observed when the bioreactors were operated under extended idle or cold temperatures. To decrease operation time and improve overall performance under these conditions, the addition of powdered activated carbon (PAC) to the bioreactors was evaluated. Three PAC dosages were studied, 1000, 2000, and 5000 mg/L, based on the influent feed volume. The highest concentration was chosen to achieve a treatment level comparable to that obtainable by a combination of biotreatment followed by a granular activated carbon column.

The glass reactors used in the study had an operating volume of 1 liter and were operated in a batch mode with a 50 percent fill volume, in which 500 mL of waste were fed to each reactor during an operating cycle. All of the reactors were seeded with activated sludge obtained from the Town of Amherst, New York POTW at an initial MLVSS concentration of 2000 mg per liter of total reactor volume. Based on an influent COD concentration of 2000 mg/L and a 50 percent feed volume, the F/M ratio was 0.5.

The operating protocol for the bioreactors was as follows: 1) waste fed to the reactors, 2) aeration started, 3) mixed liquor samples taken for total and volatile suspended solids determinations (MLSS and MLVSS) in the bioreactor, 4) bioreactors aerated for 23 hours, 5) bioreactors settled for 1 hour, 6) supernatant samples drawn for SS and chemical oxygen demand (COD) determinations, 7) supernatant decanted to the original idle reactor volume of 500 mL, 8) reactor left idle (without aeration) for six, 13, or 20 days as needed.

#### ANALYTICAL TESTS

Analytical measurements made during this study include five-day biochemical oxygen demand (BOD<sub>5</sub>), chemical oxygen demand (COD), total organic carbon (TOC), total suspended solids (SS), volatile suspended solids (VSS), and turbidity. Tests were conducted according to procedures outlined in *Standard Methods* [6]. Unless noted otherwise, all COD determinations were performed on samples that had been filtered through a glass fiber filter paper with an average pore size of 1.2 micron.

#### RESULTS AND DISCUSSION

The results of experimental studies to assess the feasibility of using intermittent bioreactors for the treatment of contaminated groundwater and leachate are presented in this section.

##### Effect of Extended Idle Time Between Bioreactor Operation

Because treatment operations at the proposed on-site facility would be expected to be intermittent, bioreactor efficiency when operated with extended idle times was evaluated. The idle time is the period between times of bioreactor operation. Three conditions were studied in the extended idle study: one react cycle per week, one react cycle per two weeks, and one react cycle per three weeks. Five bioreactors were used for the study: one for the six day idle condition while duplicate reactors were run for the 13 and 20 day idle conditions. Duplicate bioreactors were used for the 13 and 20 day idle conditions to evaluate reproducibility of the data obtained from the study bioreactors.

Presented in Figure 1 are the COD values obtained at the end of the react cycle as a function of time. Conclusions drawn from inspection of the data presented in Figure 1 are: 1) there appears to be only minor differences in COD removal efficiencies obtained after 23 hours of aeration when extended idle times are imposed on reactor op-

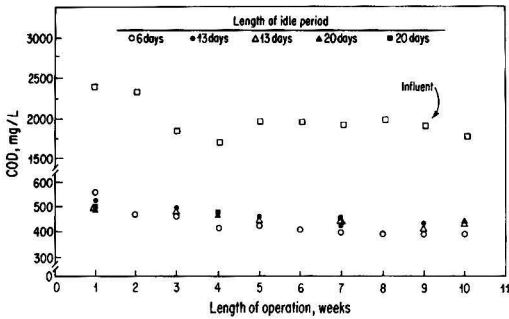


Figure 1. Effluent COD concentrations as a function of idle period duration and length of operation.

eration, 2) there is excellent reproducibility between the duplicate bioreactors used for the 13 and 20 day idle conditions and 3) the six day idle bioreactor consistently achieved the lowest effluent COD values after the first week of operation.

To determine if extended idle periods affect the time required to achieve a desired percent COD removal, COD removal as a function of react time was measured for each idle condition. As shown in Figure 2, the imposition of extended idle periods significantly impacted the rate of COD removal. Although not measured during the study, the probable cause for the degradation in reactor performance, is a reduction in the viable biomass present in the extended idle bioreactors. The major importance of the information presented in Figure 2 is the implication that, as the idle period is extended in the intermittent biological treatment process, the aeration time required to remove biodegradable COD will also increase.

To determine whether COD removal was a result of assimilation and subsequent oxidation, or uptake and storage, oxygen uptake rates were measured for the bioreactors operating during the extended idle study and compared to the COD removal trends presented in Figure 2. As presented in Table 2, the oxygen uptake rate is greatest in the initial phases of the react cycle and drops off rapidly during the aeration period for the bioreactor operating with a six day idle period. This rapid drop is common for batch operated processes and follows the trend in COD removal for that reactor. As the length of the idle period is increased, the rate of  $O_2$  uptake during the initial phase of the react cycle decreases. This decrease in initial  $O_2$  uptake is indicative of a loss of acclimation which was verified by the slower rates of COD removal in the 13 and 20 day idle reactors. For the 20 day idle period reactor the rate of  $O_2$  uptake is essentially constant for the one and six hour readings because of the slow rate of COD removal observed in that bioreactor.

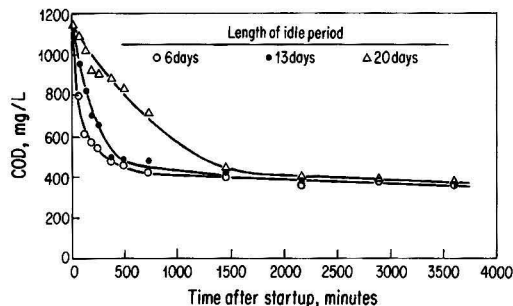


Figure 2. COD removal as a function of the time and idle period duration.

TABLE 2. OXYGEN UPTAKE RATES (MG/O<sub>2</sub>/G MLVSS-HR.) AS A FUNCTION OF REACT CYCLE TIME FOR EXTENDED LAG STUDY BIOREACTORS

Time in react cycle	Length of lag between bioreactor operation		
	6 days	13 days	20 days
1 hour	185	62	36
6 hours	14	12	34
23 hours	7.6	5.8	4.4

Oxygen uptake data can also be used to gauge oxygen supply equipment needs. If the aeration equipment is sized to meet the initial demand, some ability to reduce the supply later in the cycle may be desirable from the standpoint of energy savings. If the oxygen supply equipment is sized based on a lower rate than needed initially, then longer aeration times may be required to remove biodegradable COD.

#### Effects of Temperature on Bioreactor Performance

A study of temperature effects on the performance of the intermittent bioreactor were performed to evaluate the impact of climatic differences expected at the superfund site. For this purpose, bioreactors were operated at 5, 15, and 25°C, to determine the effect of temperature on overall effluent quality and COD removal rates. Five bioreactors were utilized for the temperature effects study. One bioreactor was operated at 25°C (room temperature), while duplicates were operated at the five and 15°C conditions. The temperature effects study was run for six consecutive weeks.

Influent and effluent COD values for each weekly react cycle are presented in Figure 3 as a function of bioreactor temperature. Observations that can be made from the data presented in Figure 3 are: 1) during the initial phase of the study effluent COD values were found to increase as the bioreactor temperature decreased; 2) as the study continued the effluent COD in all bioreactors improved; 3) performance of the two 5°C bioreactors improved at a faster rate than the 15 and 25°C bioreactors; 4) as the study continued, effluent COD in the 15°C bioreactor approached the same level of performance achieved in the 25°C bioreactor; and 5) there was excellent reproducibility between the duplicate reactors.

To determine the rate of COD removal, samples from each reactor were taken for COD analysis throughout the react cycle of the sixth operating week. As shown in Figure 4, the rate of removal was similar in the 15 and 25°C reactors while a somewhat slower rate was observed in the 5°C reactor.

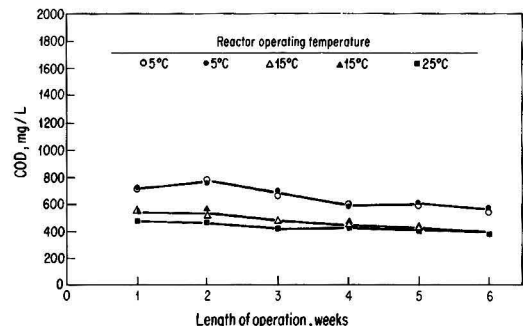


Figure 3. Effluent COD concentrations as a function of reactor operating temperature and length of operation.

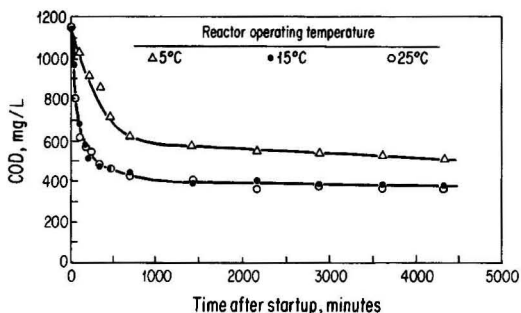


Figure 4. COD removal as a function of time and reactor operating temperature.

To further gage effluent quality, effluent suspended solids were monitored as part of the temperature study. Average suspended solids for the bioreactor based on eight observations were measured to be 262, 99, and 82 mg/L for the five, 15, and 25°C systems, respectively.

Based on the data collected as part of the temperature study the following conclusions can be made: 1) COD removal is affected by cooler temperatures; 2) the exact temperature that retards the removal of COD is unknown but lies somewhere between 5 and 15°C; 3) the biomass does acclimate to cooler temperatures as evidenced by the data in Figure 3; 4) the rate of acclimation is insufficient to negate longer aeration period requirements for cool weather operation; and 5) significant deterioration in effluent suspended solids quality occurs as bioreactor temperature is decreased.

#### Effects of Powdered Activated Carbon (PAC) Addition to the Bioreactors

Because of the long aeration times required to remove biodegradable COD under conditions of extended idle periods and reduced temperatures, further experimental studies were conducted to determine what rate advantages might be realized by supplementing the bioreactors with powdered activated carbon. In addition, depending on dosages used, elimination of the planned subsequent activated carbon columns might be made possible with the use of powdered activated carbon.

To determine the effect of PAC dosage on filterable COD removal, three concentrations were studied and compared to a control reactor operating without PAC addition. The bioreactors were operated with 50 percent feed volumes, with one react cycle per week. The PAC dosages studied were 1000, 2000, and 5000 mg/L, based on the influent feed volume. The PAC was added simultaneously with the influent waste. The PAC study was conducted over seven weeks during which time there was no wasting of solids other than those lost in the effluent.

Weekly effluent COD values from the PAC study are presented in Figure 5. Observations drawn from inspection of Figure 5 include: 1) enhanced removal of COD was observed with the addition of PAC; 2) a higher COD removal percentage was observed with increasing PAC dosages; 3) COD removal increased with study duration until an approximate equilibrium had been reached; 4) equilibrium COD values of approximately 170, 130, and 90 mg/L COD were achieved with PAC dosages of 1000, 2000, and 5000 mg/L, respectively. Equilibrium COD values plotted as a function of PAC dosage are presented in Figure 6.

Presented in Figure 7 are the data collected during the PAC study delineating the effect of PAC addition on the rate of COD removal. Removal of COD is quite rapid with baseline levels occurring in the first two to three hours of

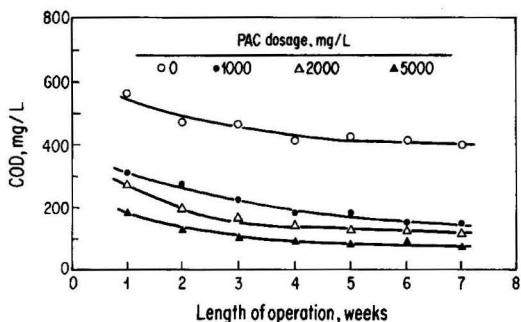


Figure 5. Effluent COD concentrations as a function of PAC dosage and length of operation.

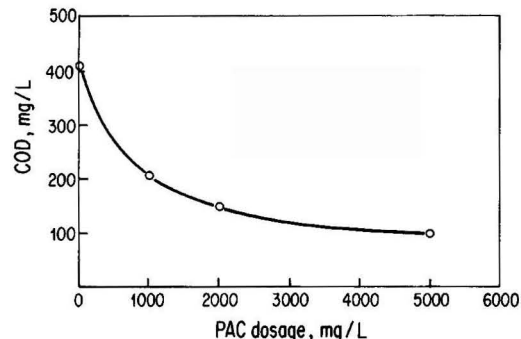


Figure 6. Effluent equilibrium COD concentrations as a function of PAC dosage.

the react cycle for the 5000 mg/L dosage. The time to reach the COD baseline increases with decreasing PAC dosage. Based on these results, it is hypothesized that the addition of PAC may significantly reduce the react time requirements for COD removal when the bioreactors are operating under periods of extended idle or extreme cold. This hypothesis is based on the assumption that a significant portion of initial COD removal observed in the PAC reactors is brought about by adsorption of organics rather than by bacterial degradation. Mechanistically, both adsorption and bacterial degradation are occurring simultaneously.

To test the above hypothesis, oxygen uptake rates were measured in a control reactor with no PAC addition, and the PAC reactors, at different times throughout the react cycle. If carbon adsorption is the major mechanism of COD removal in the initial phases of the react cycle, the

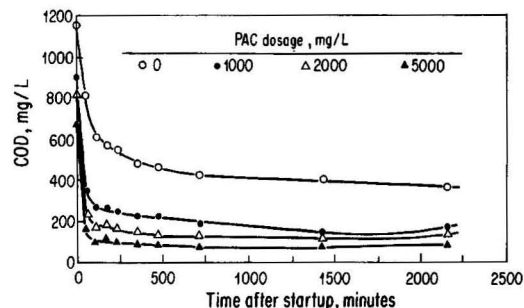


Figure 7. COD removal as a function of time and PAC dosage.

observed oxygen uptake rates should decrease as the PAC dosage is increased. In addition, O<sub>2</sub> uptake rates in the PAC reactors should be higher than endogenous rates after baseline COD values in the bioreactor are approached as adsorbed organics on the carbon continue to be biodegraded. Eventually, after the influent substrate is biodegraded, all bioreactors should approach the same endogenous O<sub>2</sub> uptake rate.

The depletion of oxygen, measured as mg O<sub>2</sub>/L-min for the PAC study bioreactors is presented as a function of time in Table 3. The reading at one hour was selected to record O<sub>2</sub> uptake during periods of rapid uptake, a measurement at six hours was selected to determine O<sub>2</sub> uptake rates in a time period when COD had reached baseline levels in the PAC reactors, but not in the control and to compare midcycle O<sub>2</sub> uptake rate with endogenous rates, and the last measurement was taken to establish endogenous O<sub>2</sub> uptake rates.

As hypothesized, the initial oxygen uptake rates for the PAC study reactors were found to be inversely proportional to the carbon dosage. This phenomenon occurs as a result of a greater fraction of the substrate partitioning on the carbon at the higher PAC dosages, reducing the amount of available substrate for bacterial degradation in the bulk fluid. At six hours, O<sub>2</sub> uptake rates for both the control and PAC bioreactors are nearly identical and are higher than the endogenous rate measured at 23 hours. Based on these results, one may postulate that the rate of bacterial degradation is similar in the control and PAC reactors even though the COD removal rates are different. This assumption seems reasonable since it is unlikely that the addition of PAC enhances the biodegradation capacity of the biomass.

The significance of these results from the point of system design is twofold: 1) because enhanced COD removal rates are likely due to adsorption of organics on the activated carbon, addition of PAC to bioreactors operating under conditions of extended lag and low temperature should improve treatment performance, and 2) because increased removal rates result from adsorption, a period continued aeration of the settled PAC bioreactor after decanting would be desirable to bioregenerate the carbon for the next react cycle.

Oxygen uptake rates for each PAC dosage at 23 hours were identical. Assuming that all biodegradable organics had been removed, it is probable that the biomass levels in the bioreactors were nearly identical. Ideally, oxygen uptake rates, should be normalized to account for the amount of biomass present in the reactor. Unfortunately, measurement of bacterial solid levels, recorded as MLVSS, is difficult in the PAC reactors because of the interference of adsorbed organics which are volatilized during the MLVSS procedure.

To further evaluate the effects of PAC addition, solids levels were monitored in the effluent from the PAC reactors. The average effluent suspended solids measured were 82, 69, 65, and 57 mg/L for 0, 1000, 2000, and 5000 mg/L PAC dosages. Qualitatively the effluent from the PAC reactors was clear, void of color, and had low turbidity. The measured values for turbidity were 12, 3, 3, and 1.5 NTUs for 0, 1000, 2000, 5000 mg/L PAC dosages.

TABLE 3. OXYGEN UPTAKE RATES (MG/O<sub>2</sub>/L-MIN.) AS A FUNCTION OF REACT CYCLE TIME FOR PAC STUDY BIOREACTORS

Time in react cycle	PAC Dosage, mg/L			
	0	1000	2000	5000
1 hour	11.1	7.8	3.9	2.8
6 hours	0.48	0.51	0.43	0.40
23 hours	0.15	0.15	0.15	0.15

TABLE 4. COMPARISON OF EFFLUENT QUALITY IN TERMS OF COD, TOC, AND BOD<sub>5</sub>

Bioreactor sample	Concentration, mg/L		
	COD <sup>a</sup>	TOC <sup>a</sup>	BOD <sub>5</sub> <sup>b</sup>
PAS waste influent	2704 <sup>c</sup>	944 <sup>c</sup>	
	2865 <sup>d</sup>	1018 <sup>d</sup>	
	1980 <sup>d</sup>		1052 <sup>d</sup>
	1889 <sup>d</sup>		1130 <sup>d</sup>
Bioreactor effluent			
— 1 React cycle per week	355	140	
	395		21.9
	412		20.7
	392		12.0
— 1 React cycle per 2 weeks	385	128	17
— 1 React cycle per 3 weeks	375	128	
— 1000 mg/L PAC, 1 React cycle per week	197	57.5	3.5
	173		<1.0
	151		5.4
— 2000 mg/L PAC, 1 React cycle per week	141	37.4	3.4
	110		2.3
	125		3.5
— 5000 mg/L PAC, 1 React cycle per week	79		1.7
	90	24.1	1.5
	91		

<sup>a</sup> Samples filtered with Whatman GF/C filter.

<sup>b</sup> Non-filtered samples.

<sup>c</sup> Pretreated influent sample.

<sup>d</sup> Non-pretreated influent sample.

#### Comparison of Effluent Quality Measures

Chemical oxygen demand (COD) was used as the primary measure of process performance and effluent quality. To determine the quality of the intermittent bioreactor effluent with other indicators of organic carbon, total organic carbon (TOC) and five day biochemical oxygen demand (BOD<sub>5</sub>) were also measured.

Presented in Table 4 is a summary of COD, TOC, and BOD<sub>5</sub> values for selected samples. It appears from the data presented in Table 3 that a bioreactor effluent of less than 30 mg/L BOD<sub>5</sub> can be achieved regardless of reactor protocol. Bioreactors with PAC addition produce the highest quality effluent in terms of BOD<sub>5</sub> with values typically less than 5 mg/L in the effluent. It is hypothesized that the majority of BOD<sub>5</sub> measured in the bioreactor effluents is brought about by respiring bacteria present in the bioreactor supernatant.

Comparison of COD and TOC values for influent and bioreactor effluent with no PAC addition produce COD/TOC ratios which range from approximately 2.5 to 3.0. This range is normal for domestic wastewater. Values for COD/TOC increase with the PAC reactors. To determine if COD/TOC ratios change throughout the react cycle for non-PAC bioreactors, C/C<sub>0</sub> values for COD and TOC were plotted as a function of time in the react cycle. As shown in Figure 8, the C/C<sub>0</sub> ratios are nearly identical for COD

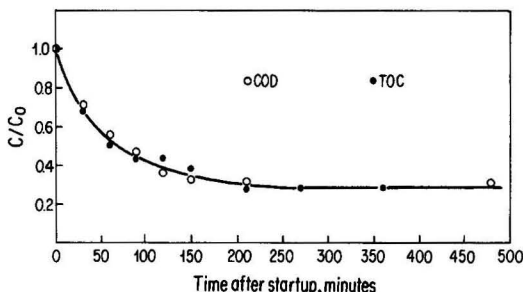


Figure 8. Comparison of COD and TOC removal as a function of time.



and TOC during the cycle. Therefore, it would appear that for the influent and bioreactors without carbon addition a nearly constant ratio exists for COD and TOC. Chemical oxygen demand is recommended as the process evaluation parameter for two reasons: 1) values for BOD<sub>5</sub> are not indicative of the true organic content; and 2) analyses for TOC require skilled personnel and expensive analytical equipment.

#### SUMMARY

An experimental study was conducted to assess the technical feasibility of biological processes treating hazardous waste when extended periods of inoperation are imposed on operation protocol. The impetus for this study was to develop a process that could provide cost effective treatment of leachate and contaminated groundwater from a former hazardous waste handling facility in Upstate New York. Waste collection rates at the site are expected to be low and as such, intermittent process operation will be desirable or necessary.

Based on the reported findings of the experimental study, intermittent biological treatment can achieve significant removal of waste pollutants. In this study the rate of COD removal was adversely affected by decreases in operation frequency and decreased operating temperatures. However, if reaction periods are extended, all biodegradable COD removal can be removed in bioreactors using long lag periods. Addition of powdered activated carbon was tested under one operating scenario and hypothesized to be advantageous in reducing aeration times for conditions of low temperature and extended lag periods.

While the feasibility of intermittent biological treatment was studied using a groundwater contaminated with hazardous waste substances, other potential applications exist. They include: 1) leachate treatment of municipal and hazardous waste landfills, industrial waste flows released on an intermittent basis, and other waste sites requiring remediation. It is hoped that the results presented in this paper, will alert others to the potential that biological systems may offer even when operating under conditions that are less than ideal.

#### ACKNOWLEDGMENTS

This study was conducted in cooperation with URS Company, Inc., Buffalo, New York and the New York State Department of Environmental Conservation (NYSDEC). John C. Goeddertz and Alan J. Rabideau, graduate students in the Department of Civil Engineering at the State

University of New York at Buffalo, provided invaluable assistance in the conduct of the experimental study. This paper was first presented at the 1986 International Conference on Innovative Biological Treatment of Toxic Wastewaters, held in Washington, D.C., June 24-26, 1986.

#### LITERATURE CITED

1. "Site Investigations and Remedial Alternative Evaluations at the Pollution Abatement Services (PAS) Site in Oswego, New York, Draft Final Report," prepared for New York State Department of Environmental Conservation by URS Company, Inc., January 1984.
2. "Experimental Investigation of Treatment Process Options for Remediation of Pollution Abatement Services (PAS) Site Groundwater," prepared for URS Company, Inc. by Department of Civil Engineering, State University of New York at Buffalo, January 1985.
3. Irvine, R. L., and W. B. Davis, "Use of Sequencing Batch Reactors for Waste Treatment—CPC International, Corpus Christi, Texas," *Proceedings, 26th Industrial Waste Conference, Purdue University, Indiana, May 1973.*
4. Irvine, R. L., S. A. Sojka, and J. F. Colaruotolo, "Enhanced Biological Treatment of Leachates from Industrial Landfills," *Proceedings, 37th Industrial Waste Conference, Purdue University, Indiana, May 1982.*
5. Herzbrun, P., M. J. Hanchak, and R. L. Irvine, "Treatment of Hazardous Wastes in a Sequencing Batch Reactor," *Proceedings, 39th Industrial Waste Conference, Purdue University, Indiana, May 1984.*
6. *Standard Methods for the Examination of Water and Wastewater*, 16th Edition, American Public Health Association, 1985.



A. Scott Weber is an Assistant Professor in the Department of Civil Engineering at the State University of New York at Buffalo. He earned a B.S. degree in Civil Engineering and an M.S. degree in Sanitary Engineering from the Virginia Polytechnic Institute and State University, and a Ph.D. in Civil Engineering from the University of California, Davis. His research interests are currently focused on the use of biological processes for the treatment of aqueous hazardous wastes.



Mark R. Matsumoto is an Assistant Professor in the Department of Civil Engineering at the State University of New York at Buffalo. He earned a B.S. degree in Civil Engineering from the University of California, Irvine, and an M.S. and Ph.D. in Civil Engineering from the University of California, Davis. His research interests are currently focused on process development of hazardous waste treatment.

# Destruction of Volatile Organic Compounds via Catalytic Incineration

**Bruce A. Tichenor**

U.S. Environmental Protection Agency  
Air and Energy Engineering Research Laboratory  
Hazardous Air Technology Branch  
Research Triangle Park, NC 27711

and

**Michael A. Palazzolo**

Radian Corporation  
Research Triangle Park, N.C. 27709

*This paper reports results from an EPA-funded study designed to investigate the effect of catalytic incinerator design and operation on the destruction of specific volatile organic compounds (VOC), both singly and in mixtures. A range of operating and design parameters were tested with a wide variety of compounds and compound mixtures. Results from the study showed that key variables affecting destruction included operating conditions (temperature, space velocity, catalyst geometry and catalyst volume), VOC composition and VOC concentration. Significant differences in destruction efficiency were found for some compounds when tested alone compared to when tested in mixtures.*

## INTRODUCTION

EPA's Air and Energy Engineering Research Laboratory conducts and sponsors research on technology to reduce or eliminate emissions of volatile organic compounds (VOC's) from industrial/commercial sources. Recently, a study on the use of catalytic oxidation to destroy VOC's (including potentially toxic air pollutants) was completed by Radian Corporation under an EPA contract. The study was designed to investigate the effect of catalytic incinerator design and operation on the destruction of specific VOC's, both singly and in mixtures. A range of operating and design parameters were tested on a wide variety of compounds and compound mixtures. This paper presents the results of this research effort.

## BACKGROUND

Catalytic incinerators are used by a variety of industrial sources to reduce VOC emissions. Several catalyst formulations are sold for VOC control, although precious metal catalysts (e.g., platinum or palladium) predominate. Fixed bed systems with various geometries are available,

as are fluidized bed units.

A recent EPA study summarizes the application of catalytic incineration in the US [1]. While it has been estimated that over 500 catalytic units are operating in the US, the study identified only 149 specific facilities which employed catalytic systems for VOC control. These systems were distributed across the following industrial categories:

Solvent/Coating Application and Drying - 60%  
Organic Chemical Production - 15%  
Miscellaneous Processes - 25%

Field data were collected at eight incinerators in the Solvent/Coating industrial category. These data indicated that the design efficiency for VOC combustion was achieved at five of the installations. Two of the incinerators had deactivated catalysts and achieved poor destruction. The remaining unit also showed low efficiency, but the space velocity was excessive.

EPA has also conducted tests of a pilot scale catalytic incinerator on the emissions from a flexographic printing press and a full scale unit on a formaldehyde plant [2]. The pilot scale tests were conducted over a range of tem-

peratures and space velocities. The results, shown in Figures 1 and 2, indicate that total VOC destruction efficiency exceeded 95% over the range of test conditions. The results also show that the destruction efficiency of specific compounds (e.g., propyl acetate and heptane) varied considerably from the total destruction under some conditions. Eight tests were conducted on the formaldehyde plant over a 10-month period. All the tests showed VOC destruction of 98% or higher.

## PURPOSE OF THE STUDY

An evaluation of the literature on catalytic incineration [1] and the EPA testing previously conducted (see above) provides substantial information on the performance of catalytic systems. This information covers a multitude of catalyst materials and geometry, operating conditions, and VOC compounds and concentrations. Unfortunately, the information is insufficient to allow one to predict confidently the performance of a given catalytic incinerator applied to a specific VOC mixture. Only via ad hoc laboratory or pilot tests can such data be obtained.

The purpose of the study reported herein [3] was to conduct a comprehensive evaluation of catalytic incineration of VOC's to determine the effect of operating parameters (i.e., temperature and space velocity) and VOC waste stream characteristics (i.e., concentration, compound type, and mixture composition) on the destruction of specific organic compounds. The study was designed to identify the effects, not to determine their cause. It was hoped that the results of the study would assist in focusing future research on the most critical questions.

## EXPERIMENTAL DESIGN

### Test System and Methods

The test system consisted of a skid-mounted catalytic incineration unit and a solvent vapor generation system. The skid-mounted unit, which was leased from Englehard Industries, was equipped with a blower, preheater, mass flowmeter, catalytic reactor, and temperature controls. A schematic diagram of the catalytic incineration unit is shown in Figure 3. Gases from the solvent generation system were metered into the unit at flowrates ranging from 3.4 to 17 m<sup>3</sup>/hr. Prior to entering the catalyst bed, the gases were heated to the desired temperature with a controlled electric preheater. The electric preheater consisted of a pipe or tube wrapped with an electrical resistance heater element. Test compounds were oxidized on the catalyst bed, and the exhaust was vented. Heat loss from the catalyst bed was minimized by a second electric heater controlling the temperature of the catalyst shell.

Catalyst beds tested consisted of ceramic honeycombs coated with precious metal (platinum/palladium) catalyst. The beds were cylindrical in shape with a 3.8 cm diameter and either a 15 or 30 cm length. Space velocities tested with the catalysts ranged from 15,000 to 80,000 hr<sup>-1</sup>, and catalyst inlet temperatures tested ranged from 260° to 425°C.

Spiked air streams for testing were generated by evaporating liquid organic compounds into a clean air stream at a controlled rate. Gas samples were withdrawn from the incinerator at three locations: the inlet of the incinerator, the outlet of the electric preheater, and the outlet of the catalyst bed. Concentrations of VOC's present in these samples were determined by two independent methods. Individual compound concentrations were determined by gas chromatography and flame ionization detection (GC/FID, EPA Method 18). Calibration gas mixtures for the GC/FID analysis were prepared dynamically using the same system used in preparing the spiked air streams. Total non-methane hydrocarbon (NMHC) concentrations were also determined by flame ionization detection (modified EPA Method 25A). Total NMHC concentrations were quantified against propane standards.

### Experimental Design

Achieving the objective of this study required the selection of a wide range of incinerator operating conditions. Major operating parameters that were varied during the testing included catalyst inlet temperature, compound concentration, space velocity, compound type, catalyst geometry, and catalyst volume. Much of the testing was conducted to characterize compound destruction across the heater and catalyst bed as a "system." However, heater and catalyst destruction efficiencies were also measured separately under a large number of conditions. Test parameters and the range of conditions tested are shown in Table 1.

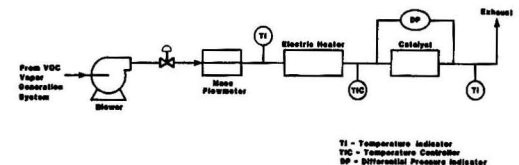


Figure 3. Catalytic incineration unit schematic.

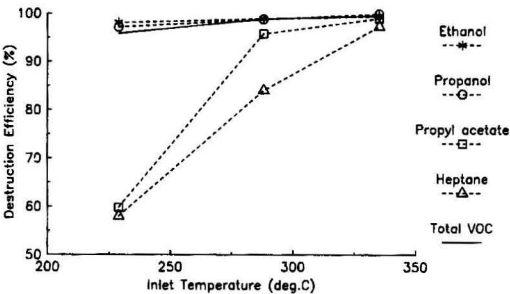


Figure 1. Destruction efficiency for flexographic printing emissions vs. temperature (space velocity = 50,000/hr).

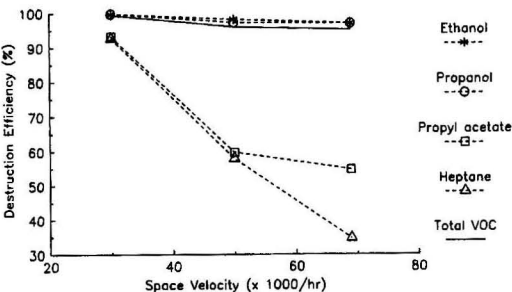


Figure 2. Destruction efficiency for flexographic printing emissions vs. space velocity (temperature = 230 deg. C).

TABLE 1. TEST PARAMETERS AND CONDITIONS FOR VOC/HAP COMPOUNDS

Test Parameter	Conditions or Values Tested
VOC/HAP Mixture	8 multicomponent mixtures and 16 single components <sup>a</sup>
Total Mixture Inlet Concentration (ppmC) <sup>b</sup>	10,000 6,000 1,200
Space Velocity (hr <sup>-1</sup> ) <sup>c</sup>	15,000 20,000 30,000 33,000 50,000 80,000
Catalyst Inlet Temperature (°C)	260 360 280 370 305 400 315 425 345
Catalyst Geometry/Volume (cm <sup>3</sup> ) <sup>d</sup>	Geometry A/170 Geometry A/340 Geometry B/170

<sup>a</sup>Components in the tested mixtures are shown in Table 2.

<sup>b</sup>This is the concentration at the inlet of the electric preheater in parts per million as carbon.

<sup>c</sup>Based on total catalyst volume and gas flowrate at standard conditions (20°C and 1 atm).

<sup>d</sup>The larger catalyst volume was achieved by doubling the length of the catalyst while maintaining the same cross-sectional area.

A total of eight multicomponent mixtures with between two and seven compounds each were tested. In addition, 16 of the compounds were tested singly. Compounds in each of the mixtures are shown in Table 2. Mixtures 1, 1A, 1B, and 1C were used to investigate the effect of combining several compound classes. Mixture 2 represents a typical industrial solvent emission. Mixtures 3, 4, 5 and 6 combined several compounds from one or two classes and Mixtures 7 and 8 were selected to represent hazardous air pollutant (HAP) emissions.

## RESULTS

Results from the study provide data showing the effect of incinerator operating conditions and VOC waste gas characteristics on compound specific and overall mixture destruction efficiency. These data are summarized in this section.

### Operating Conditions

As expected, compound specific and overall mixture destruction efficiencies were found to be strongly influenced by catalyst inlet temperature and space velocity. Figures 4 and 5 illustrate the effect of these two parameters on the destruction efficiency of selected mixtures. The data in Figures 4 and 5 show that the destruction efficiency of some mixtures are more strongly influenced by inlet temperature and/or space velocity than others.

For the particular catalytic unit tested under this study, compound destruction in the gas preheater often contributed significantly to the overall "system" (i.e., catalyst plus preheater) destruction efficiency. Relative contributions of preheater and catalyst destruction efficiencies for Mixture 1 are shown in Figure 6. The degree to which heater destruction efficiencies observed during this study may represent heater or burner zone destruction

TABLE 2. COMPONENTS IN MULTICOMPONENT VOC/HAP MIXTURES

Mixture 1-Control Mixture	Mixture 4-Ketones/ Miscellaneous Oxygenated Compounds
iso-Propanol Methyl ethyl ketone Ethyl acetate Benzene n-Hexane	Acetone Methyl ethyl ketone Methyl isobutyl ketone Cyclohexane Ethyl Cellosolve Dioxane
Mixture 1A-Hexane Substitution	Mixture 5-Aldehydes
iso-Propanol Methyl ethyl ketone Ethyl acetate Benzene Cyclohexane	Propionaldehyde iso-Butyl aldehyde iso-Valeraldehyde n-Butyl aldehyde n-Valeraldehyde
Mixture 1B-Hexane Substitution	Mixture 6-Alkanes/Aromatics
iso-Propanol Methyl ethyl ketone Ethyl acetate Benzene iso-Octane	n-Hexane n-Octane n-Decane Benzene Toluene m-Xylene iso-Propyl benzene
Mixture 1C-Hexane Substitution	Mixture 7-Non-Chlorinated HAP's
iso-Propanol Methyl ethyl ketone Ethyl acetate Benzene n-Octane	m-Cresol Acrylonitrile
Mixture 2-Industrial Mixture	Mixture 8-Chlorinated HAP's
Methyl ethyl ketone Toluene	Methylene chloride Carbon tetrachloride Ethylene dichloride Trichloroethylene Tetrachloroethylene 1,1-Dichloroethane 1,1,2-Trichloroethane
Mixture 3-Alcohols/Acetates	
Methanol Ethanol iso-Propanol n-Butanol Ethyl acetate n-Propyl acetate iso-Butyl acetate	

efficiencies on full-scale catalytic incinerators is not known. Most full-scale incinerators requiring waste gas preheat employ natural gas preheaters instead of electrical resistance heaters. Compound destruction in these natural gas preheaters may vary considerably depending on the preheater design.

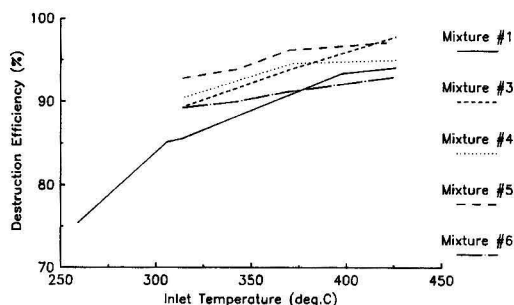


Figure 4. Effect of temperature on destruction efficiency (space velocity = 50,000/hr).

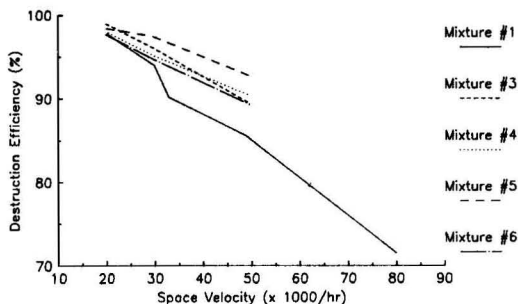


Figure 5. Effect of space velocity on destruction efficiency (temperature = 315 deg. C).

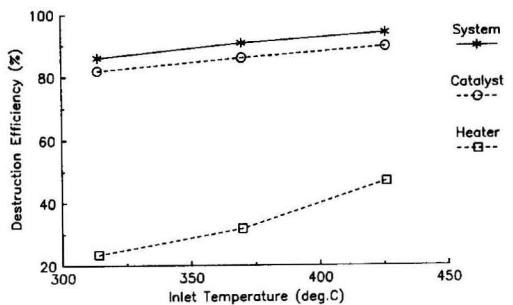


Figure 6. Relative contribution of heater and catalyst to system destruction efficiency (mixture no. 1; space velocity = 50,000/hr).

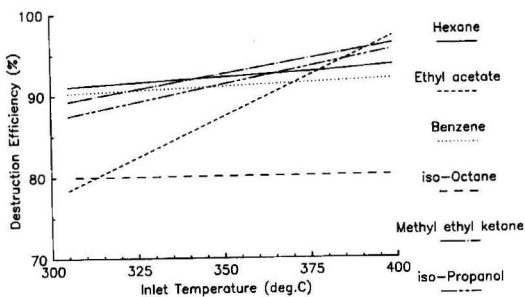


Figure 7. Destruction efficiency for single compounds vs. temperature (space velocity = 50,000/hr).

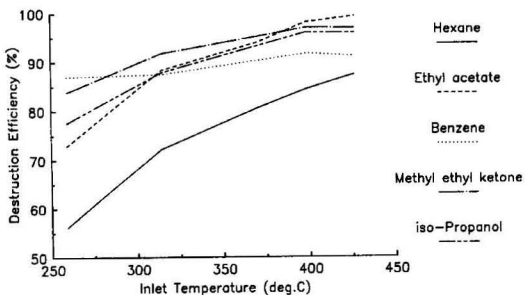


Figure 8. Destruction efficiency for compounds in mixture no. 1 vs. temperature (space velocity = 50,000/hr).

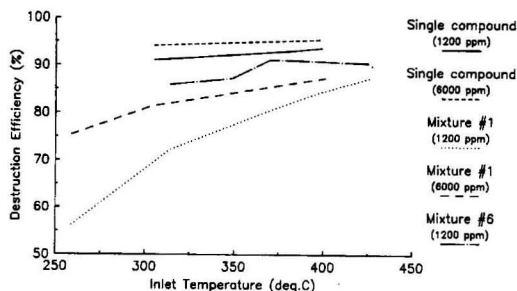


Figure 9. Destruction efficiency for n-Hexane vs. temperature (space velocity = 50,000/hr).

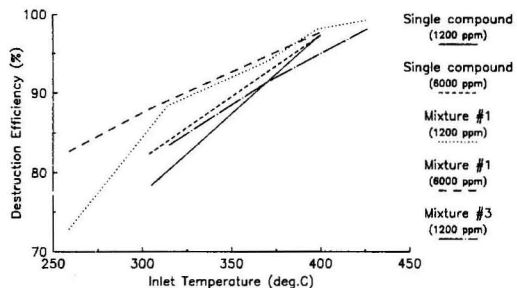


Figure 10. Destruction efficiency for ethyl acetate vs. temperature (space velocity = 50,000/hr).

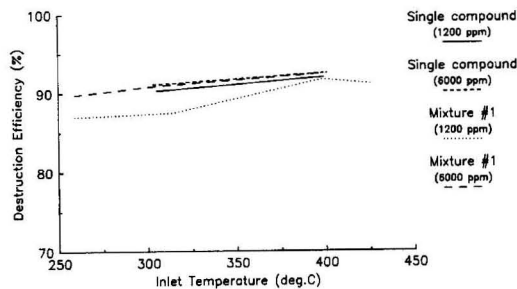


Figure 11. Destruction efficiency for benzene vs. temperature (space velocity = 50,000/hr).

Other test results relating to incinerator operating conditions showed the importance of catalyst geometry and catalyst volume. For one test series, catalyst surface area was increased by reducing the honeycomb cell size and in another test series, the catalyst volume was increased by doubling the catalyst length. Both the increased surface area and the increased volume resulted in improved destruction efficiency, with the greatest improvement occurring at low temperatures and high space velocities.

#### VOC Composition/Concentration

The effect of VOC concentration was evaluated by testing Mixture 1 and the single compounds in Mixture 1 at total concentrations of 1,200 and 6,000 ppmv. The results indicated that higher concentrations did result in slightly higher compound destruction efficiencies. This

effect was more evident at low temperatures (305°C) than at higher temperatures (400°C).

The *effect of compound class* was determined by comparing the destruction efficiencies of various compounds and compound classes at given combinations of temperature, space velocity, and VOC concentration. This comparison provided the following ranking of compound classes:

Compound Class	Relative Destructibility
Alcohols	<div style="text-align: center;">           High            ↓            Low         </div>
Cellosolves/dioxane	
Aldehydes	
Aromatics	
Ketones	
Acetates	
Alkanes	
Chlorinated hydrocarbons	

All of the compound classes, except chlorinated hydrocarbons, were able to be destroyed with 98-99% efficiency at sufficiently low space velocities/high temperature. A destruction efficiency of 97% was achieved for acrylonitrile and cresol (Mixture 7). It should be noted that the ranking provided above is generally applicable to classes of compounds; specific compounds within each class may exhibit different relative destructibilities when compared to other compounds within the same or different classes.

The destruction efficiency for the chlorinated hydrocarbons was quite low. In addition, tests conducted after the chlorinated hydrocarbon "burns" showed that the catalyst had been partially deactivated.

The *effect of compound mixtures* is best illustrated by comparing the destruction efficiencies of specific compounds when tested alone vs. their destruction when tested in mixtures. If the "mixture effect" were negligible, these efficiencies would be similar. Figure 7 shows the results of tests conducted on single compounds at 1200 ppmv. Note that significant differences exist between the individual destruction efficiencies. Figure 8 shows the results of testing these same compounds (except iso-octane) in a mixture at 1200 ppmv. As in the single compound tests (Figure 7), there are obvious differences between the destruction efficiencies for the individual compounds. It is noted, however, that the compound destruction for some of the compounds is quite different when Figures 7 (single compounds) and 8 (mixture) are compared. For example, hexane achieved greater than 90% destruction at 305°C when incinerated alone (Figure 7), but was less than 75% destroyed at the same temperature when combusted in a mixture (Figure 8). This effect is further illustrated in Figure 9, which clearly shows that hexane is more effectively destroyed when incinerated by itself. Figure 9 also shows that the type of mixture has an effect; note that the efficiency reduction is much less for Mixture 6 (alkanes and aromatics) than for Mixture 1 (five compound classes). The "mixture effect" is not consistent between compounds. Figure 10 shows that the destruction of ethyl acetate was greater when burned in a mixture than by itself. Finally, some compounds showed no effect; benzene, for example, showed no differences in destruction efficiencies due to mixture (see Figure 11).

## CONCLUSIONS

The following conclusions are based on the results discussed above. While some may be applicable to catalytic incineration of VOC's in general, they are presented here as applying only to the test catalyst and ranges of conditions tested:

- (1) VOC compound destruction efficiency increases with increasing temperature and decreasing space velocity.
- (2) VOC compound destruction efficiency increases with increasing concentration.
- (3) The destructibility of VOC's varies according to compound class.
- (4) Individual VOC's have different destruction efficiencies (at a given concentration, temperature, and space velocity).
- (5) Different destruction efficiencies may be obtained for a specific VOC incinerated in a mixture vs. when burned alone.

## LITERATURE CITED

1. Jennings, M. S., N. E. Krohn and R. S. Berry, "Control of Industrial VOC Emissions by Catalytic Incineration," Report No. EPA-600/2-84-118a-i, July 1984.
2. Martin, N. A., "Catalytic Incineration of Low Concentration Organic Vapors," Report No. EPA-600/2-81-017 (NTIS No. PB81-158446), February 1981.
3. Palazzolo, M. A., J. I. Steinmetz, D. L. Lewis, and J. F. Beltz, "Parametric Evaluation of VOC/HAP Destruction via Catalytic Incineration," Report No. EPA-600/2-85-041 (NTIS No. PB85-191187/A7), April 1985.

**Bruce A. Tichenor** is an Environmental Engineer in the Hazardous Air Technology Branch of the U.S. EPA Air and Energy Engineering Research Laboratory, Research Triangle Park, North Carolina. In this position, he is responsible for directing research on the assessment and control of organic air pollutants. He received his B.S. in Civil Engineering and Ph.D. in Sanitary Engineering from Oregon State University. Prior to coming to North Carolina in 1979, he worked at EPA's research laboratory in Corvallis, Oregon where he was involved in a wide variety of projects relating to assessment and control of water pollution. He is a registered Professional Engineer in the state of Oregon.



**Michael A. Palazzolo** is a Staff Engineer with Radian Corporation in Research Triangle Park, N.C. He is responsible for providing managerial and engineering support for research programs in the areas of VOC control, hazardous and municipal waste incineration and flue gas desulfurization. He has a Bachelor of Science degree in Chemical Engineering from the University of Michigan.



# Operating and Testing a Combined SO<sub>2</sub> and NO<sub>x</sub> Removal Facility

Norman W. Frank, Gary A. Miller, and David A. Reed

Ebara International Corp., Hempfield Industrial Park, Greensburg, PA 15601

*Test results and operational procedures of a 32,000 Nm/hr combined SO<sub>2</sub> and NO<sub>x</sub> removal facility utilizing electron beam technology and dry ammonia injection are discussed in detail, showing how the facility can be operated to give maximum removal efficiencies and optimum utility requirements. To date, the overall plant design efficiencies of 90% SO<sub>2</sub> and NO<sub>x</sub> removal efficiency have been achieved. A brief history of the development of the process along with a description of the plant is presented. Performance of the plant is compared to previous similar pilot plants operated in Japan and the influences of process parameters on the plant operation and removal efficiencies are discussed. Use of an alternative reagent and its effect on removal efficiencies and plant operation is presented followed by results of analysis of the fertilizer by-product yielded by the process.*

## INTRODUCTION

It has been recognized by the coal consuming community that federal emission limits for stationary sources have become progressively more stringent over the years and a continuation of this trend can be expected for the future. Since most present-day SO<sub>2</sub> and particulate control systems have evolved in response to a particular environmental regulation mandating control of one particular pollutant, these same systems tend to lose flexibility and become less economical to operate as old regulations are tightened or as new regulations are promulgated. For example, regulations mandating additional decreases in SO<sub>2</sub> content in flue gases for existing plants would be satisfied by either additional control equipment or reduced boiler outputs at the expense of increased capital costs or reduced capacity. In the event that passage of regulations controlling nitrogen oxides (NO<sub>x</sub>) emissions becomes a reality, most single species desulfurization systems cannot remove NO<sub>x</sub> without expensive add-on processes. This type of approach often results in increasing mechanical and operational complexity of the control system, multiple waste and/or product streams, decreased availability and crowded siting in areas of the plant where space is already at a premium.

*This report was prepared by Ebara International Corporation (EIC) in cooperation with and sponsored by Indiana Power and Light Company (IPALCO) and the U.S. Department of Energy (DOE). Neither EIC, IPALCO nor DOE nor any person acting on behalf of them: (1) makes any warranty or representation, express or implied, with respect to the use of any information, apparatus, method or process disclosed in this report or that such use may not infringe on privately owned rights; or (2) assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this report.*

An alternative to these existing control systems is the Ebara Electron Beam Flue Gas Treatment Process (E-Beam FGT). Utilizing a method of simultaneous desulfurization and denitrification of combustion flue gases, this process promises to gain swift acceptance by both utility and industrial coal consumers and enable further growth in the use of both medium and high sulfur coals. Among the E-Beam FGT's unique features are included:

- Simultaneous removal of SO<sub>2</sub> and NO<sub>x</sub> at high removal efficiencies
- A dry process which involves no slurry recycling, no sludge disposal and no gas re-heat
- Excellent turndown and load-following capabilities with a minimum of process control
- Simple operation yet flexible enough to treat a wide range of inlet SO<sub>2</sub> and NO<sub>x</sub> concentrations at high efficiencies without costly modifications
- Lack of by-product processing enables scrubber siting in areas of restricted space
- Pollutants are converted into a single easily handled product stream
- Conversion of SO<sub>2</sub> and NO<sub>x</sub> into a salable nitrogen fertilizer

In 1983, Ebara International Corporation, under a cost-sharing agreement with the U.S. Department of Energy, embarked upon a program to build a demonstration plant for this process in the United States. Also participating in the program are the Indiana Energy Development Board, Indiana Electric Association-Member Companies, Amax Coal Company and C. F. Industries. The primary purpose of the program is to demonstrate the feasibility of the Ebara E-Beam FGT process to remove simultaneously 90% of the SO<sub>2</sub> and NO<sub>x</sub> in medium and high sulfur coal-fired boiler flue gases while operating the Process Demonstration Unit (PDU) over an extended period. Current testing, aimed at optimizing SO<sub>2</sub> and NO<sub>x</sub> simultaneous

removal efficiencies, will be followed by by-product optimization runs and duration/availability testing.

The purpose of this report is to serve as a follow-up to the paper given at the 1985 AIChE Spring National Meeting and to present the results of some of the removal efficiency optimization runs conducted to date. Comparisons of the PDU operation will be made with previous pilot plants operated in Japan. The effects of process parameters and flue gas composition on individual and simultaneous  $\text{SO}_2$  and  $\text{NO}_x$  removal efficiencies will be examined as well as their impact on utilization of the process for commercial plants.

### BRIEF DEVELOPMENT HISTORY

Ebara began the development of this process in Japan in the early 1970's. Two pilot plants, one treating 1,000  $\text{Nm}^3/\text{hr}$  of oil-fired boiler flue gases and the other treating 10,000  $\text{Nm}^3/\text{hr}$  of iron-ore sintering machine flue gases, have been successfully operated in Japan. The first pilot plant was constructed at Fujisawa, Japan and was successfully operated from 1974-77. Heavy oil combustion gas containing 230 ppm  $\text{SO}_2$  and 240 ppm  $\text{NO}_x$  was continuously treated yielding over 80% removal of  $\text{NO}_x$  and almost 90% removal of  $\text{SO}_2$  at electron beam dosages of 2.5-3.5 Mrad. Particles produced during the process operation were collected by an electrostatic precipitator, analyzed and found to contain both sulfur and nitrogen. The plant was operated both with and without ammonia injection with highest removal efficiencies being recorded with ammonia addition.

Based on the favorable experimental and operational experience on the Fujisawa plant, a second pilot plant was constructed at the Nippon Steel Corporation Works at Wakamatsu, Japan. This facility successfully treated 10,000  $\text{Nm}^3/\text{hr}$  of iron-ore sintering exhaust gases from 1977 thru 1978, removing more than 90% of the  $\text{SO}_2$  and 50%  $\text{NO}_x$  at a 1.0 Mrad dose and a 0.8 ammonia stoichiometry. When the dosage was increased to 1.5 Mrads, the  $\text{SO}_2$  and  $\text{NO}_x$  removal efficiencies were maintained at levels of 95% and 65% respectively although  $\text{NO}_x$  removal efficiencies of 90% were subsequently recorded at ammonia stoichiometries of 1.0 and reaction temperatures of 77°C. Upon x-ray diffraction analysis, the by-product was shown to be composed of ammonium nitrate and ammonium nitrate-sulfate mixed crystal.

### BRIEF PDU PLANT DESCRIPTION

The site plan for the PDU is shown in Figure 1. A sidestream of flue gas from the coal-fired boiler is extracted, analyzed for  $\text{SO}_2$  and  $\text{NO}_x$  content and fan drafted to the inlet of the spray cooler. As the gas passes through the cooler, atomized water is sprayed into the gases to reduce its temperature to optimum levels in preparation for irradiation. Specially designed controls enable cooling of the gases down to within 16°C of the water dew point without wet bottom operation of the cooler. An upstream ammonia injection port is located in the flue gas ductwork just prior to the entry of the cooled flue gas into the process building.

In addition to the process vessel, the process building also houses all the electron beam equipment. A cutaway of the building is shown in Figure 2. The electron beam system used in the PDU consists of two 80 kW units operating at 800 kV. Each unit has a dedicated power supply consisting of an insulating core transformer and DC auxiliary equipment taking conventional 460 volt, three phase power as service power. Each power supply is cable connected to its electron accelerator/scanner package. This package is mounted integrally on a rolling cart and track system which includes a concrete "plug" door as part of the protection against generated secondary x-rays. This

arrangement was adopted to allow maximum serviceability of the E-beam while retaining the overall smallest process vessel/E-beam package for an aboveground plant concept. The two guns are horizontally opposed and vertically offset to provide maximum flue gas energy absorption. This absorbed energy is expressed in terms of Megarads (Mrads) of equivalent energy equaling approxi-

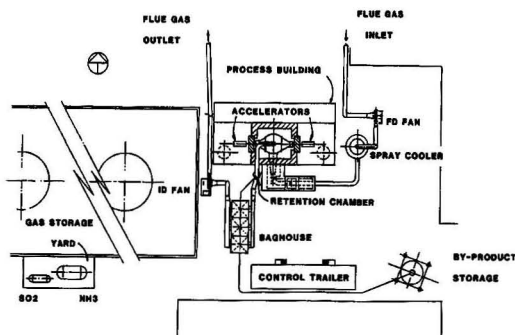


Figure 1. PDU site plan.

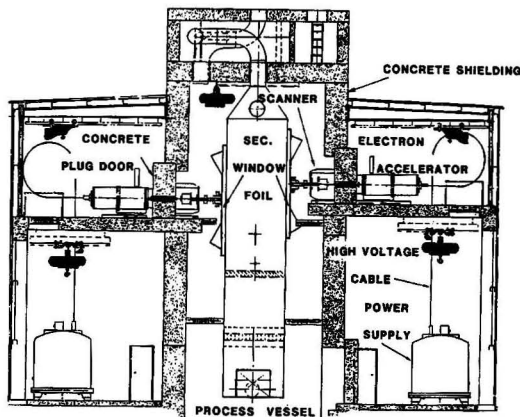


Figure 2. Process building cutaway.

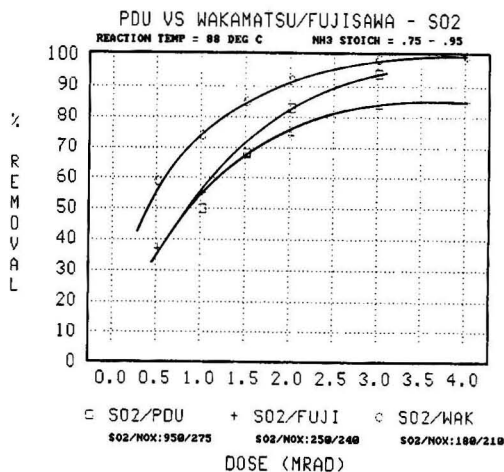


Figure 3.  $\text{SO}_2$  removal efficiencies.



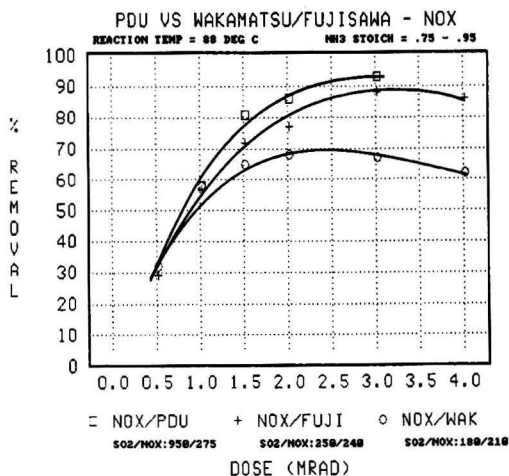


Figure 4. NO<sub>x</sub> removal efficiencies.

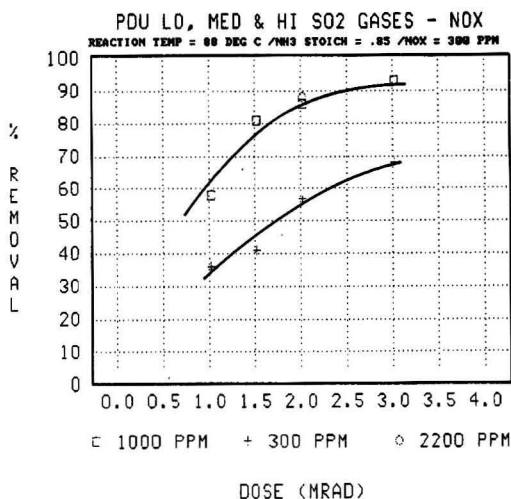


Figure 6. NO<sub>x</sub> removal efficiency vs. gas SO<sub>2</sub> content.

mately 10 J/g of flue gas per Mrad. Since this absorbed energy is the beam delivered energy minus its transmittance and scattering losses, for constant accelerating voltages and flue gas flow rates the dose rate is always proportional to the total beam current. An Ebara designed secondary window foil system separates the primary window foil in the scanner from contact with abrasives and corrosives in the flue gas. The secondary window foil also allows the exchanging of a failed secondary window foil by remote control with a minimum of off-line time.

After the inlet ductwork enters the process building vault area, the flue gas flows into the process vessel inlet. As a final preparation before entering the irradiation zone, the flue gas mixture is further humidified by the Pre-Reaction Gas Cooling System which again uses atomized water droplets to control the gas temperature rise associated with the exposure to the electron beam as well. Once in the irradiation zone, the humidified gas mixture is subjected to an intense field of energized electrons which collide with the flue gas molecules resulting in molecular ionization. These ions interact with the flue gas

constituents resulting in the creation of free atoms and radical species such as O<sup>+</sup> and OH. These are capable of rapid reaction with the SO<sub>2</sub>, NO<sub>x</sub> and water in the flue gas to yield ultimately a fine mist of sulfuric and nitric acids in the process vessel which, in turn, is neutralized when mixed with the injected ammonia vapor. As the mixture exits the process vessel, it passes the secondary downstream ammonia injection port and enters the retention chamber. At this point, the ammonium nitrate and ammonium nitrate-sulfate particles have already started to form.

Passing through the retention chamber, the ammonium nitrate and ammonium nitrate-sulfate crystals in the treated flue gas are allowed to agglomerate to the appropriate size required for efficient removal by the baghouse. In the baghouse, this by-product is separated from the flue gas with the now clean flue gases reinjected back to the boiler stack through the induced draft fan. The collected by-product powder is pneumatically transported from the baghouse hoppers through insulated lines for storage in a heated silo for removal off-site.

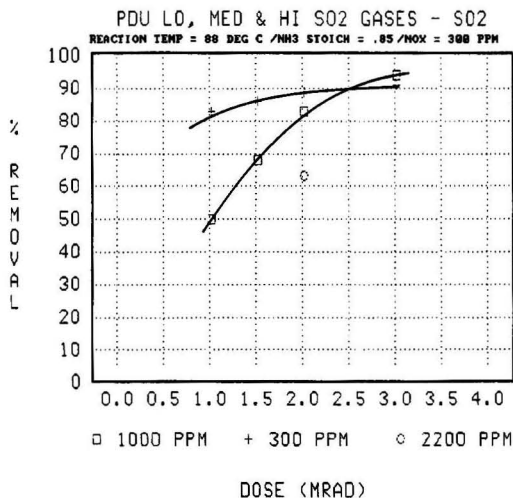


Figure 5. SO<sub>2</sub> removal efficiency vs. gas SO<sub>2</sub> content.

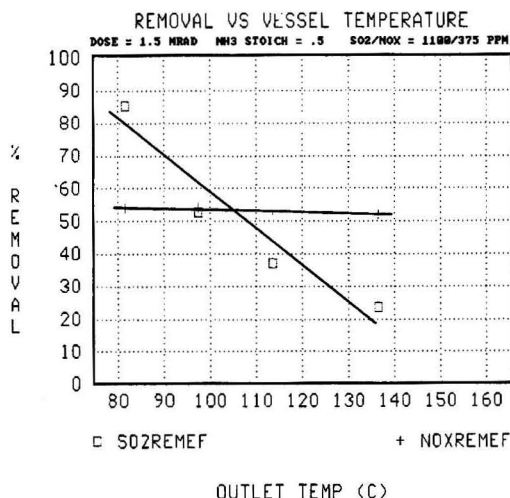


Figure 7. SO<sub>2</sub> and NO<sub>x</sub> removal vs. vessel temperature.

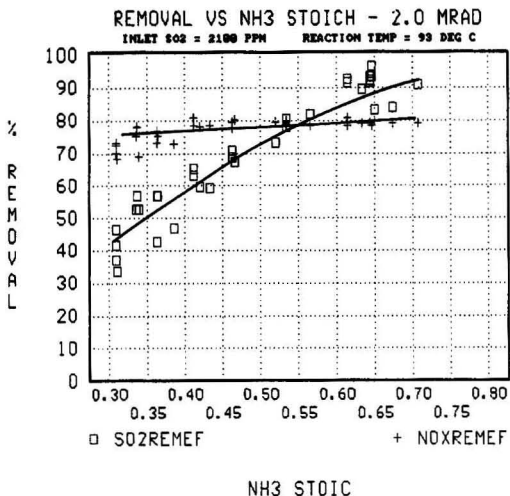


Figure 8. SO<sub>2</sub> and NO<sub>x</sub> removal vs. NH<sub>3</sub> stoichiometry.

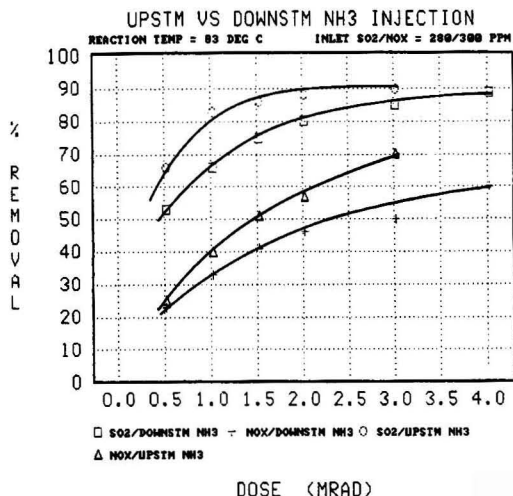


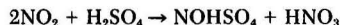
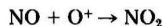
Figure 9. Effect of NH<sub>3</sub> injection location.

## RESULTS

### PDU Plant Results with NH<sub>3</sub> as Reagent

Operation and testing of the PDU has demonstrated that the operability and performance of the process to be comparable to the previous pilot plants at Fujisawa and Wakamatsu. Figures 3 and 4 show a comparison of SO<sub>2</sub> and NO<sub>x</sub> removal efficiencies for these two plants and the PDU under similar operating conditions. As expected, both SO<sub>2</sub> and NO<sub>x</sub> removal efficiencies showed a strong dependence on beam dose rate. For SO<sub>2</sub> removal, the PDU outperformed the Fujisawa plant performance at dose rates over 1.5 Mrads. Performance against the Wakamatsu plant was not as high as expected, however, SO<sub>2</sub> removals did approach the Wakamatsu data as the dosage was increased towards 3 Mrads. This, in all likelihood, was caused by the operation of the PDU with medium sulfur flue gas (SO<sub>2</sub> content equal to 1000 ppm) while the Wakamatsu plant operated on lower sulfur flue gas (SO<sub>2</sub> content equal to 300 ppm). In addition, differences in process equipment, in part due to efforts to increase the NO<sub>x</sub> removal efficiencies in the PDU, could also have been a contributing factor and will be the topic of further testing later in the program. Comparisons of the NO<sub>x</sub> removal efficiencies indicate superior removal performance by the PDU over both the Fujisawa and the Wakamatsu plants by substantial margins. Overall, the project goal of simultaneous removal efficiencies in excess of 90% for SO<sub>2</sub> and NO<sub>x</sub> has been accomplished with the PDU.

Figures 5 and 6 show the results of testing the PDU on different coal sulfur compositions at constant ammonia stoichiometries. As can be seen, both SO<sub>2</sub> and NO<sub>x</sub> removal efficiencies show strong dependencies on the flue gas sulfur content. SO<sub>2</sub> removal efficiencies at any particular dose tended to decrease nonlinearly with increasing sulfur content. However, increased flue gas sulfur content boosted NO<sub>x</sub> removal efficiencies dramatically showing again a nonlinear effect throughout the entire range of tested dosages. These results generally support findings from the Wakamatsu pilot plant tests in which SO<sub>2</sub> removal rates generally increase with flue gas absorbed dosages while NO<sub>x</sub> removals tended to increase with increasing flue gas sulfur content. Since increases in SO<sub>2</sub> content in the flue gases yield increases in the quantities of sulfuric acid droplets for a given dose, oxidation and reduction of NO<sub>x</sub> is enhanced through the following reactions:



In addition to increased production of secondary nitric acids, increased sulfuric acid concentrations should also tend to enhance the formation of the mixed crystal due to higher rates of absorption of the nitric acid droplets into the sulfuric droplets. Testing is continuing on enhancement of the crystal formation and with higher sulfur coals to support further these findings. Preliminary data showing removal efficiencies from higher sulfur equivalent coal runs are indicated on the graphs for 2200 ppm SO<sub>2</sub> content flue gas.

### INFLUENCE OF PROCESS PARAMETERS

As part of scheduled testing, the influence of many process parameters on the operation and performance of the process has been evaluated. Among these are included the process temperature at the exit of the process vessel (reaction temperature) and the role of ammonia injection in maximizing removal efficiencies. Figures 7 and 8 summarize some of the results of these tests. Figure 7 shows the effects of reaction temperature on SO<sub>2</sub> and NO<sub>x</sub> removal efficiencies at constant ammonia stoichiometry and dose. The SO<sub>2</sub> removal efficiency rises rapidly as the reaction temperature decreases while the NO<sub>x</sub> removal efficiency shows only a small increase. This indicates that process temperature can be used effectively to increase SO<sub>2</sub> removal efficiency with minimal impact on the NO<sub>x</sub> removal rate. A second parameter which may be used to increase SO<sub>2</sub> removal efficiency is the ammonia injection rate or stoichiometry. Figure 8 shows the effect on both SO<sub>2</sub> and NO<sub>x</sub> removal efficiencies with varying ammonia reagent flow rates expressed as a function of the ideal chemical stoichiometry or stoichiometric ratio of ammonia to flue gas quantity, SO<sub>3</sub> content, inlet SO<sub>2</sub> and NO<sub>x</sub> concentrations. Results are shown for high sulfur equivalent flue gas and illustrate again that for a given dose, the addition of small amounts of ammonia enhances SO<sub>2</sub> removal efficiency with SO<sub>2</sub> removal being proportional to the amount of ammonia injected. NO<sub>x</sub> removal efficiencies show very little dependence on the rate of ammonia addition instead showing again, for a given SO<sub>2</sub> concentration, the characteristic single dependence on beam dose rate alone.

TABLE I. REPRESENTATIVE BY-PRODUCT ANALYSIS—AMMONIA REAGENT

Ion	Wt %*	Mol %
SO <sub>4</sub> <sup>-2</sup>	64.0	34.6
NH <sub>4</sub> <sup>+</sup>	21.9	63.0
NO <sub>3</sub> <sup>-</sup>	2.9	2.4

\*of soluble product

The testing conducted at the Wakamatsu pilot plant included evaluation of the most beneficial location for ammonia injection to maximize removal efficiency. Injection ports were provided both immediately upstream of the process vessel enabling flue gas irradiation in the absence of or in the presence of ammonia. As such, similar testing was conducted at the PDU, the results of which are presented in Figure 9. As can be seen, higher SO<sub>2</sub> and NO<sub>x</sub> removal efficiencies were recorded for all dose rates with upstream ammonia injection which is in basic agreement with the Wakamatsu results.

**RESULTS OF BY-PRODUCT ANALYSIS**

As a part of the test program, numerous samples of the generated by-product have been taken for chemical and ion analysis. A representative analysis of these samples is presented in Table I. Referring to the mol ratio of NH<sub>4</sub>/SO<sub>4</sub>, roughly a 2:1 ratio was consistently recorded implying the presence of ammonium sulfate. Subsequent x-ray diffraction and chemical analysis confirmed the main constituent to be ammonium sulfate with small amounts of ammonium nitrate.

The small amount of ammonium nitrate consistently found in the by-product samples was surprising and as such will be one of the focuses of the by-product optimization testing previously mentioned.

**PDU PLANT RESULTS WITH NaOH AS REAGENT**

As part of the continuing effort Ebara is directing toward making the E-Beam FGT more flexible and cost ef-

fective, testing, has been conducted with alternative reagents in lieu of the anhydrous ammonia used in both Fujisawa and Wakamatsu pilot plants. One of these reagents recently tested was a solution of water and sodium hydroxide (NaOH). Referring to Figure 1, the hydrated NaOH was injected into the spray cooler in place of the cooling water thus enabling the tower to act as a spray dryer. Since both the spray nozzle and liquid delivery systems and controls were not optimized for this service, SO<sub>2</sub> removals attributable to the dryer were low, measuring approximately 30%. As Figure 10 indicates, however, increasing beam dosage yielded almost linearly increasing SO<sub>2</sub> removal efficiencies. NO<sub>x</sub> removal efficiency increased also as dose increased, though at lower absolute values. Overall, at an injection rate of 15 kg/hr of NaOH, over 70% of the SO<sub>2</sub> and 40% of the NO<sub>x</sub> was removed from the flue gases. At higher reagent feed rates SO<sub>2</sub> removal efficiencies were boosted yielding in excess of 90% removal at a 3.2 Mrad dose rate as shown in Figure 11. It should be noted that unlike the ammonia based E-Beam FGT process, removal efficiencies with the sodium hydroxide based process did not appear to be sensitive to reaction temperature through process vessel outlet temperature ranging from 68 to 107°C.

**CONCLUSION**

The PDU has been successfully operated yielding results for the most part comparable to or exceeding those of the two previous pilot plants. Among the most notable of these results are:

- Simultaneous SO<sub>2</sub> and NO<sub>x</sub> removals in excess of 90%
- SO<sub>2</sub> removal shown to be dependent on dose and ammonia quantity while NO<sub>x</sub> removal shown to be a function of dose alone. Both SO<sub>2</sub> and NO<sub>x</sub> were shown to respond in inverse proportion to reaction temperature with SO<sub>2</sub> removals having the most pronounced effect.
- Successful application to low, medium and high sulfur coal flue gases with high SO<sub>2</sub> and NO<sub>x</sub> re-

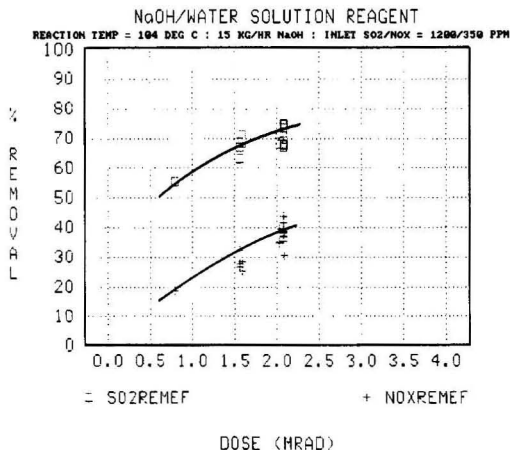


Figure 10. Low concentration NaOH/water solution.

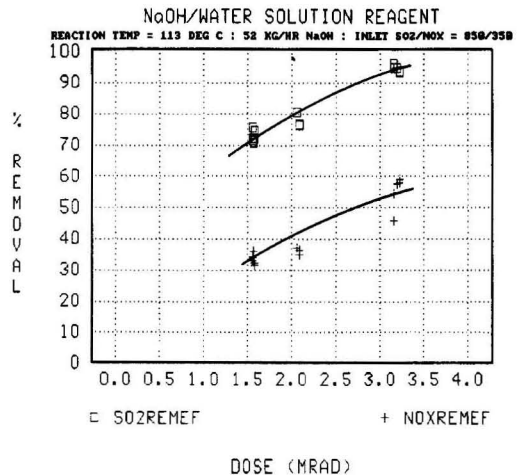


Figure 11. High concentration NaOH/water solution.

moval efficiencies—adjustment of either ammonia injection flow or beam dose can be used to favor the removal of either pollutant or to maximize simultaneous removals.

Additional testing will determine optimum modes for by-product generation, operability and general plant availability information.

The Ebara E-Beam FGT process offers considerable promise for simple removal of  $\text{SO}_2$  and  $\text{NO}_x$  at high efficiencies. Presently, while government regulations are focused primarily on  $\text{SO}_2$  control, the advantages that the process enjoys of combined  $\text{SO}_2$ ,  $\text{NO}_x$  and fine particulate control over other systems will become more and more appealing as increasingly stringent government controls are imposed.



**G. A. Miller**, Senior Engineer in the Process Design and Development Section of Ebara International Corporation, earned his B.S. Degree in Mechanical Engineering at Virginia Polytechnic Institute. Currently he is a member of the design and testing teams for the PDU facility.



**D. A. Reed**, Chemical Engineer for Ebara International Corporation, earned his B.S. Degree in Chemical Engineering at the University of Maryland. Currently he is working with the operations and maintenance section at the demonstration unit in Indianapolis, Indiana.

# H<sub>2</sub>S/SO<sub>2</sub> Removal in the Modified-Claus Reaction Over Packed Alumina Beds

C.-L. (Joe) Chou

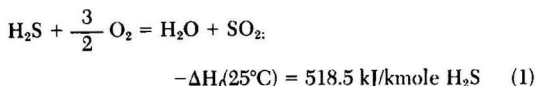
Aluminum Company of America, Alcoa Laboratories, Alcoa Center, PA 15069

*The removal of H<sub>2</sub>S and SO<sub>2</sub> by the modified-Claus reaction was studied in a computer-controlled packed bed system over activated alumina catalyst. The reactor system consisted of two 6.35 × 60.96 cm reactors in parallel and was designed to allow for the axial temperature monitoring and side stream sampling. The H<sub>2</sub>S/SO<sub>2</sub> conversion efficiencies were evaluated against gas-hourly space velocity (GHSV) ranging from 100 to 12,000 1/hr at the three typical Claus converter conditions for three sizes of Alcoa S-100 Claus catalyst. The conditions for defining the kinetic and thermodynamic regimes of the modified-Claus reaction were reported. The thermodynamic regime was checked and confirmed by the equilibrium predictions of a computer program utilizing the principle of minimization of Gibbs free energy. The possible rate-controlling mechanism in the kinetic regime and the effects of water vapor on the reaction were discussed.*

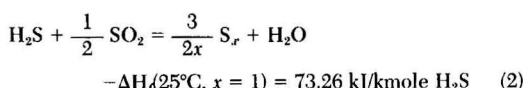
## INTRODUCTION

The Claus process is an efficient way of removing hydrogen sulfide from acid gas streams and it has been widely practiced in industries such as natural gas processing, oil refining, synfuel processing, and metal smelting. The original Claus process involves the partial oxidation of H<sub>2</sub>S in a single step over a catalyst at 200-350°C. Because of the strongly exothermic heat of reaction involved, the original process is limited to very low space velocities of the H<sub>2</sub>S-containing streams.

The modified Claus process, in use for almost a half century, significantly increases the gas processing capacity by dividing the Claus process into two steps. The first step is the complete oxidation of one-third of the H<sub>2</sub>S to SO<sub>2</sub> in a free-flame reaction furnace according to the following reaction:



The remaining two-thirds H<sub>2</sub>S is then allowed to react with SO<sub>2</sub> in a 2 to 1 stoichiometric ratio over a catalyst, producing elemental sulfur:



The reaction is commonly carried out in two or three catalytic converters in series at temperatures between 180°C

and 380°C. Usually, a total of 94% to 98% of sulfur can be recovered, depending upon the H<sub>2</sub>S concentration of the acid gas. The unconverted sulfur gases are either passed through a tail gas clean-up unit for further reduction of sulfur species or incinerated before being discharged to the atmosphere.

Increasingly strict pollution control regulations require maximum sulfur recovery from the Claus unit in order to minimize sulfur containing effluent. Increasing the sulfur conversion efficiency of the Claus unit should significantly reduce the burden and, therefore, the cost of operating the tail-gas unit, if it is needed. Among the many factors that could affect the conversion efficiency of the Claus process, catalyst activity plays a major role.

Many materials reportedly catalyze the modified-Claus reaction. Those which have been lab-tested include activated alumina, activated bauxite, zeolite, cobalt-molybdate on alumina, activated carbon, iron oxide, zinc oxide and metal sulfides [1, 2, 3, 4]. Due to its high conversion efficiency, better mechanical properties and most important, long life and low cost, activated alumina is the one most widely used in industry. Parallel to the H<sub>2</sub>S/SO<sub>2</sub> reaction in converters, activated and promoted aluminas were also reported to convert COS and CS<sub>2</sub> efficiently [5, 6, 7].

Although the activity of activated alumina for the H<sub>2</sub>S/SO<sub>2</sub> reaction has been reported previously [3, 4, 8], most of the work was conducted in small reactors containing only a few grams of ground catalyst. Such data are generally good for intrinsic kinetic studies, but do not represent realistic conversion performance of the catalysts, which should include the effects of physical transport processes. This paper reports the performance of Alcoa commercial activated alumina catalysts for the modified-Claus reaction (Eq. 2) in packed beds which were operated at conditions simulating plant converters.

C.-L. (Joe) Chou is presently with IMC Inc., 1331 South First St., Terre Haute, IN 47808.

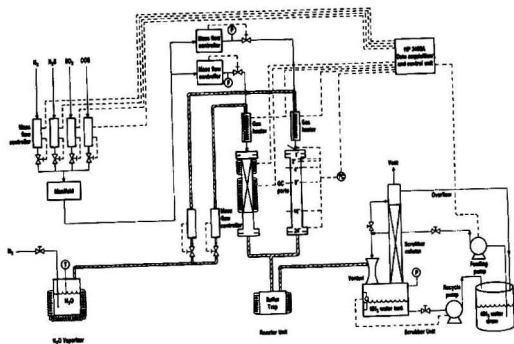


Figure 1. Schematic diagram of Alcoa Packed-Bed Claus Reactor System.

The tests were also extended to extremely high space velocity in order to determine the limit of reaction equilibrium so that the kinetic and thermodynamic regimes of the catalysts could be defined.

## EXPERIMENTAL

The Claus system used in this study is a computerized reactor system with two packed beds and is expandable to operate four beds simultaneously. As shown in Figure 1, it mainly consists of a gas feeding unit, a reactor unit, a scrubber unit and a data acquisition/control unit.

The desired flow rates are measured before mixing the gases in a surge tank. The mixed gases are split equally into two streams. The gases pass through Sylvania gas heaters and are heated to the desired temperature before entering the top of the reactor. The reactor is a 2.5 × 24 inch (6.35 × 60.96 cm) SS-316 tube, packed with a catalyst 16 inches (40.64 cm) in depth. Each reactor is equipped with 7 thermocouple wells which are located at the inlet and 1, 2, 4, 8, 16, and 24 inches of the bed height. GC sampling ports are located at the inlet and 4, 8, and 16 inches of the bed height. Each reactor is heated by two, separately controlled, heating tapes.

The size of reactors was chosen based on the following general criteria. First, the reactor has to be long enough so that the influence of axial dispersion on steady-state conversion can be neglected. It has been shown that in steady-state isothermal operation at  $Re > 20$ , the axial dispersion effects can be neglected so long as the length of the reactor is greater than 50 particle diameters [9]. In the case of nonisothermal operation, the length/particle diameter ratio has to increase by three fold in order to account for the three-fold decrease in axial thermal Peclet number. Secondly, the diameter of the reactor has to be at least 10 times the particle diameter so that the influence

of radial dispersion and the wall can be minimized. This is based on the fact that radial Peclet number is about 5 to 6 times greater than that of axial dispersion, which means radial profiles are less easily damped by dispersion than the axial profiles. As a result, the ratio for the reactor diameter is 5 to 6 times smaller than that for the reactor length. The catalysts used in this study, which are 1/4-inch (6.4-mm) or less in diameter, were well within the sphere size range for which the reactor was designed.

After passing through the bed, the reactant gases entered a heated sulfur trap where elemental sulfur, one of the products, was condensed. The gases were then passed through a scrubber unit before being vented to the atmosphere. The scrubber unit consists of a venturi for the initial removal of the sulfur gases and a packed column for the complete removal of subsequently escaped sulfur gases. The absorption agent, 30% ammonia in water, was circulated between a drum and the scrubber column.

The Claus system is controlled by a HP 3490A data acquisition/control unit through a HP 9826 computer with a screen display and a printer. The data acquisition unit records thermocouple temperature and gaseous flow rate readings every two minutes. The gases were manually sampled through the four GC ports. An HP 5830A gas chromatograph with thermal conductivity sensor and Supelco's Super Q column was employed for determining conversion efficiency. The column, a 1/8-inch (0.318-cm) OD, 6-foot (183-cm) stainless steel tube with 80/100 mesh packing, was operated at 140°C and was found to give satisfactory performance after purging with air at 100°C for 30 minutes.

For the runs involving water vapor in the inlet gas stream, nitrogen was passed through a water vaporizer to pick up moisture. The amount of water vapor delivered to the reactor was controlled by the temperature of water in the vaporizer and the flow rate of nitrogen that passed through it. It has been found that saturation of water vapor in the nitrogen stream was easily achieved. The reactions with 1% H<sub>2</sub>S, 0.5% SO<sub>2</sub> and water vapor of 10, 20, and 30% at and below 220°C were investigated. Since it has been reported that the presence of water vapor in sampling bottles may change equilibrium concentrations of sulfur species, the gas samples were passed through a phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>) bed to remove the water vapor before being analyzed by GC. Agreed with what has been reported, the P<sub>2</sub>O<sub>5</sub> bed did not seem to adsorb any of the sulfur species.

Physical and chemical properties of Alcoa 3/16-inch S-100 activated alumina are shown in Table I [10]. A typical pore size distribution of S-100 is shown in Fig. 2.

Before being loaded into the bed, the catalysts were preconditioned in a furnace for 16 hours at 350°C in order to stabilize the change of surface area which would otherwise occur in the reaction. The surface area was reduced approximately 5-10% after preconditioning. The bed was then pretreated with SO<sub>2</sub> gas at 300°C for 3 hours in order to reduce the transient period of the subsequent Claus reaction (SO<sub>2</sub> adsorption is a slower step). At the end of each run, the bed was purged with N<sub>2</sub> gas at 300°C for 1 hour to remove any sulfur that might have condensed in the pores of catalysts.

Since the catalysts were not expected to deactivate in a short time, the same catalysts were used repeatedly until the bed was changed out for a new experiment. For the bed of 1/4-inch S-100, the top and bottom samples were analyzed for surface area, pore size distribution and sulfur content. It should be noted that the catalysts were preconditioned and remained in the reactors for about one month at temperatures between 200°C to 350°C. During the one-month period, the catalysts were exposed to sulfur gases of varying concentrations for a total of about 100 hours.

TABLE I. TYPICAL PHYSICAL AND CHEMICAL PROPERTIES OF 3/16" (4.8 MM) S-100 CALUS CATALYST

Surface area	340 m <sup>2</sup> /g
Total pore volume	0.55 cm <sup>3</sup> /g
Alumina XRD phase	Amorphous, chi, and gamma
Crush strength	55 lbs (25 kg)
Abrasion loss	0.1 wt%
Loose bulk density	45 lbs/ft <sup>3</sup> (0.72 g/cm <sup>3</sup> )
	wt%
Al <sub>2</sub> O <sub>3</sub>	95.1
SiO <sub>2</sub>	0.02
Fe <sub>2</sub> O <sub>3</sub>	0.02
Na <sub>2</sub> O	0.30
LOI (250°-1200°C)	4.5

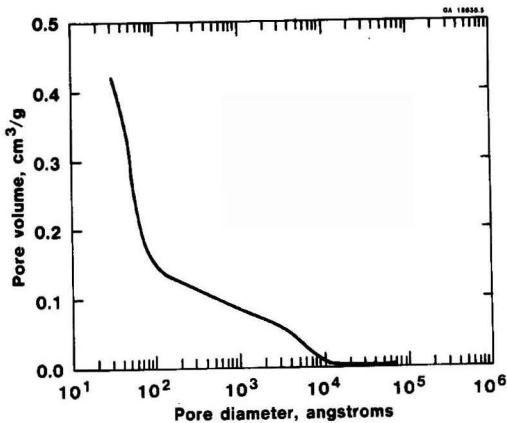


Figure 2. Pore volume distribution of S-100 Claus catalyst.

Nitrogen adsorption analysis on the top and bottom samples showed that surface area of the used samples changed very little, as compared with that of preconditioned samples. Pore size distributions of the used samples were seen identical to that of the preconditioned samples. This indicated that pore structure of the Claus catalysts was not altered as a result of one-month experiment under temperatures. Chemical analysis of the sulfur content in the used catalysts showed that no "free" sulfur was found and the level of sulfated sulfur was less than one weight percent. Viewing that very little changes in physical and chemical properties of the Claus catalysts, along with the fact that it takes a few years to observe the deactivation of catalysts in industrial practice, the loss of catalyst activity should not be a concern in this study.

The experimental conditions used to this study to simulate Claus plant conditions were:

- First Converter: 320°C, 7.5% H<sub>2</sub>S/3.75% SO<sub>2</sub>;
- Second Converter: 275°C, 2.0% H<sub>2</sub>S/1.0% SO<sub>2</sub>; and
- Third Converter: 220°C, 1.0% H<sub>2</sub>S/0.5% SO<sub>2</sub>.

A range of gas-hourly space velocity (GHSV) from 100 to

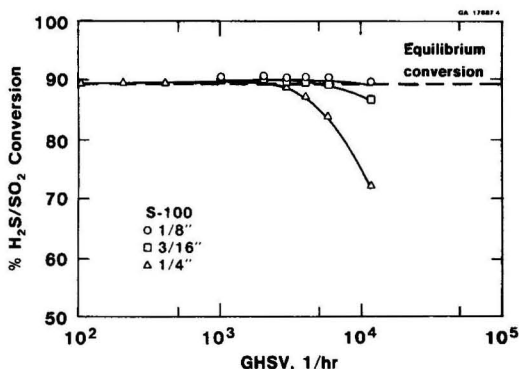


Figure 3. Effects of GHSV on the H<sub>2</sub>S/SO<sub>2</sub> conversion efficiency for three sizes of S-100 catalyst. First converter: 320°C, 7.5% H<sub>2</sub>S/3.75% SO<sub>2</sub>.

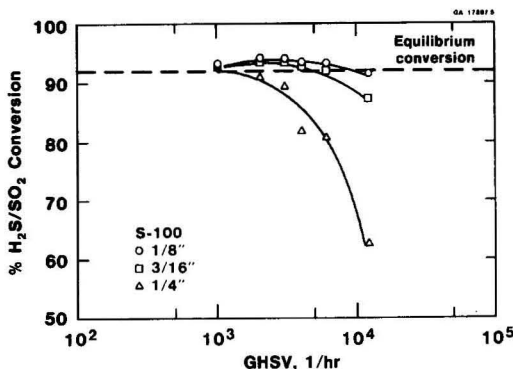


Figure 4. Effects of GHSV on the H<sub>2</sub>S/SO<sub>2</sub> conversion efficiency for three sizes of S-100 catalyst. Second converter: 275°C, 2.0% H<sub>2</sub>S/1.0% SO<sub>2</sub>.

12,000 hr<sup>-1</sup> was studied to examine the effects of space velocity on conversion efficiency, using Alcoa's three different sizes of S-100 catalyst. A few runs involving water vapor were extended to below sulfur dew point to examine the effects of water vapor on the low-temperature Claus reaction.

The axial temperature profile of the bed, as measured by the six thermocouples located at the center of the reactors, can be adjusted by three temperature controllers; i.e., inlet gas heater, and the top and bottom reactor heaters. It is difficult to maintain isothermal conditions for packed beds of the sizes used in this study, especially under first converter conditions. The objective of the temperature control is to achieve an isothermal profile in the axial direction of the bed. If that is not possible, then the profile should resemble that of a plant, an operation where the bed temperatures are adjusted to rise gradually and level off at some bed height close to the entrance. Experiments showed that except for the entrance, the axial temperature variation of the first converter reaction was within ±5°C. Where the reaction is less vigorous, as in the third converter, a temperature profile with ±1°C variation was achieved. The temperatures at bed heights of 4, 8, and 16 inches where the gases were sampled are all very close to the desired temperatures.

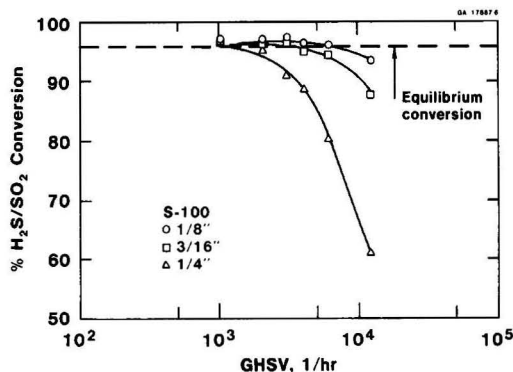


Figure 5. Effects of GHSV on the H<sub>2</sub>S/SO<sub>2</sub> conversion efficiency for three sizes of S-100 catalyst. Third converter: 220°C, 1.0% H<sub>2</sub>S/0.5% SO<sub>2</sub>.

## RESULTS AND DISCUSSION

### Effect of GHSV and Size of Catalyst

Results on the conversion efficiency as a function of gas-hourly space velocity (GHSV) are shown in Figures 3 to 5 for the three converter conditions. Three sizes of Alcoa S-100—1/4 inch (6.4 mm), 3/16 inch (4.8 mm), 1/8 inch (3.2 mm)—are compared. GHSV was defined as the number of empty bed volume that reactant gases traversed per hour and was based on the standard temperature and pressure. It should be noted that the data for the 1/4-inch S-100 catalyst in Figure 3 are the results of three experiments at overall GHSV of 100, 1000, and 3000  $\text{hr}^{-1}$ . Side-stream sampling generated additional data points at two and four times the overall GHSVs. For example, the conversion of the gas sampled at an 8-inch bed height was treated as that at 2000 GHSV when the experiment was run at 1000 overall GHSV (based on 16-inch bed height).

Conversion efficiency was defined as the fraction of total inlet concentration of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  which was decomposed to elemental sulfur. The theoretical conversion efficiency, shown by dashed lines, was calculated by an equilibrium program, SOLGASMIX, available at Alcoa Laboratories that uses the principle of minimization of Gibbs free energy. The program can handle five elemental sulfur species in the gas phase: i.e.,  $\text{S}_2$ ,  $\text{S}_5$ ,  $\text{S}_6$ ,  $\text{S}_7$  and  $\text{S}_8$ . It also allows for the removal of liquid sulfur at temperatures below the sulfur dewpoint. The computer predictions, slightly lower than those experimentally majored, are based on one atmosphere pressure. The program predicts equilibrium conversion efficiencies of 89.5%, 92.0% and 95.8% for the first, second, and third converter conditions shown above.

Figure 3 clearly shows that for GHSV up to 3000  $\text{hr}^{-1}$  there is no significant difference in conversion efficiency for the three sizes of S-100 catalyst under first converter conditions. Each reaches the theoretical conversion efficiencies. It should be noted that no data were taken for 1/8 and 3/16-inch S-100 at GHSV lower than 1000, because thermodynamic conversions were expected. As GHSV is increased beyond 3000  $\text{hr}^{-1}$ , conversion efficiencies for 1/4-inch S-100 declined, while those for 1/8-inch and 1/16-inch S-100 remain at the theoretically predicted levels. At 12,000 GHSV, absolute conversion efficiency for 1/4-inch S-100 is about 72%.

As already known, the equilibrium conversion is not affected by the physical properties of the catalysts. However, in the kinetic regime of the Claus reaction, the conversion could be affected by the size and pore structure of the catalysts. In that regime, as one might expect, decreasing catalyst size increases conversion efficiency. There seems to have been a great increase in the conversion efficiency between the 1/4- and 3/16-inch catalysts. As catalyst size further decreases to 1/8 inch, conversion efficiencies are only slightly increased since the measured conversions are approaching the theoretical conversion.

Similar results were obtained for second and third converter conditions, as shown in Figures 4 and 5. For GHSV of approximately 2000 and below, measured conversion efficiencies remain at the level predicted by thermodynamics. Beyond that, 1/4-inch S-100 shows much faster decrease in conversion efficiency than the other two sizes. However, the difference in absolute conversions efficiencies between the second and the third converter is much less than that between the first and the second converter. The absolute conversion efficiency of 1/4-inch S-100 at 12,000 GHSV is about the same, 61%, for the second and the third converter, compared to 72% for the first converter.

If the same data are plotted in terms of absolute conversion efficiency versus reaction temperature using GHSV

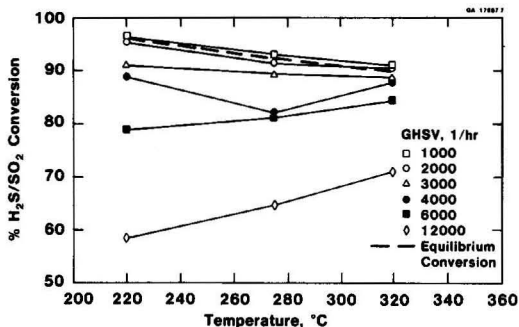


Figure 6. Effects of temperature on the  $\text{H}_2\text{S}/\text{SO}_2$  conversion efficiency at various GHSVs for 1/4" S-100 Claus catalyst.

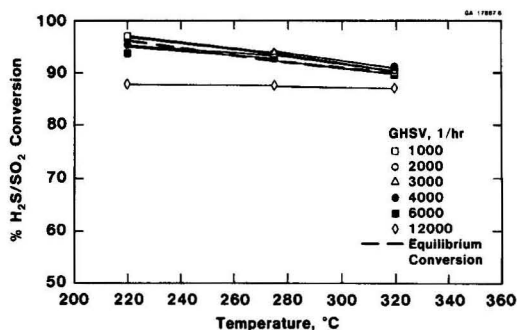


Figure 7. Effects of temperature on the  $\text{H}_2\text{S}/\text{SO}_2$  conversion efficiency at various GHSVs for 3/16" S-100 Claus catalyst.

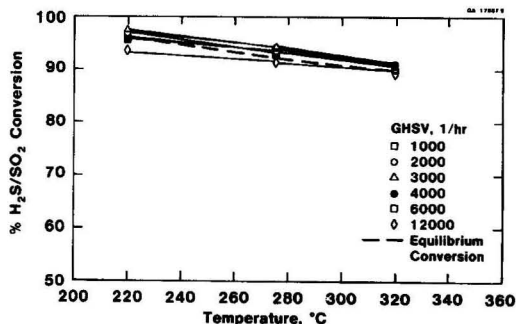


Figure 8. Effects of temperature on the  $\text{H}_2\text{S}/\text{SO}_2$  conversion efficiency at various GHSVs for 1/8" S-100 Claus catalyst.

as a parameter, the effect of temperature becomes more obvious. Shown in Figures 6, 7, and 8 are such plots for three sizes of S-100. As seen in Figure 6, increasing the GHSV will reduce the conversion efficiency of the 1/4-inch S-100 catalyst. The effect is more prominent at lower temperatures since the rate process, either reaction rate or diffusion rate, is slower at lower temperatures. At low GHSVs, the conversion efficiencies are seen to be decreasing with increasing reaction temperature, as predicted by thermodynamics. This indicates that the reaction at low GHSVs is thermodynamically limited. On the other hand, at high GHSVs the conversion increases with



increasing temperature. This clearly indicates that the reaction is limited by kinetics. The switch from thermodynamic limitation to kinetic limitation occurs at about 2000 to 3000 GHSV. Although the switch occurs at lower GHSVs for the reaction at lower temperatures, the temperature effects are not very significant.

The performance of 3/16-inch S-100, as shown in Figure 7, is different from that of 1/4-inch S-100. Except for 12,000 GHSV, the data points are all close to the theoretical line, which means that for 3/16-inch S-100 the kinetic limitation of the Claus reaction is not shown until the GHSV reaches as high as 12,000. For the 1/8-inch S-100 in Figure 8, one can see that almost all the data points fall into the neighborhood of the theoretical conversions. It clearly indicates the performance advantage for the smaller size Claus catalysts.

The rate of a heterogeneous catalytic reaction is determined by a combination of serial and parallel rate steps. The rate steps are mainly composed of bulk diffusion, pore diffusion and intrinsic kinetics. It has been found in this study that changing gas flow rate, keeping GHSV constant, has little effect on the conversion efficiency. Thus, the factor of bulk diffusion may be eliminated. Also it is well known that the Claus reaction is a fairly fast reaction and the conversion efficiency measured under high GHSVs improved only slightly at increased temperature, as opposed to the strong temperature dependency of intrinsic kinetics. Therefore, it is likely that the overall rate is controlled by pore diffusion in a larger sphere for catalytic reactions under extremely high space velocity. This has been confirmed by our experimental results on the size effect. If intrinsic kinetics were the controlling step, no size effect should be observed for the reaction at the same temperature and space velocity.

The rate of pore diffusion can be affected by pore structure and catalyst size. Pore structure may be characterized by the void fraction and tortuosity factor, both of

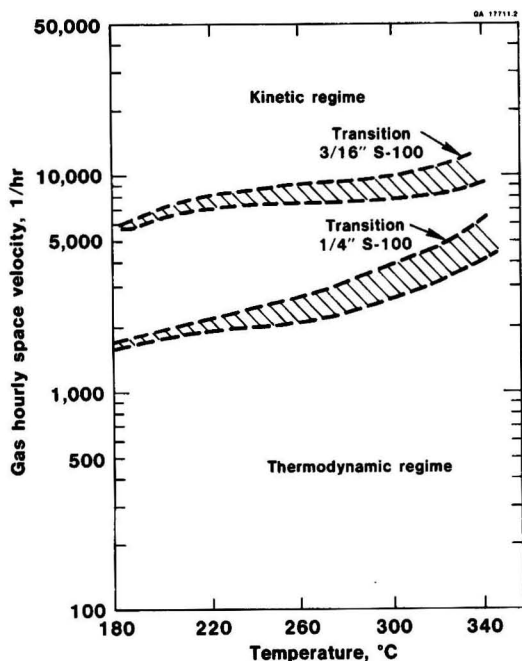


Figure 9. Kinetic and thermodynamic regimes of the H<sub>2</sub>S/SO<sub>2</sub> reaction for 1/4" and 3/16" S-100 Claus catalyst.

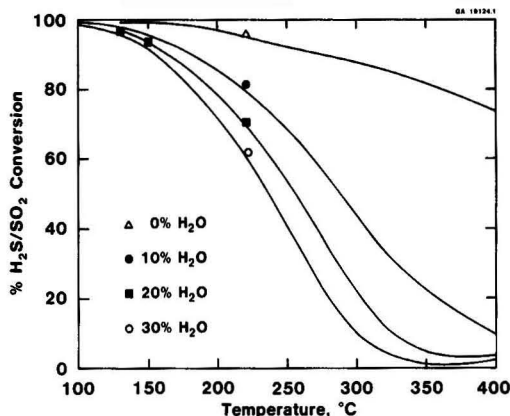


Figure 10. Comparison of theoretical predictions (lines) and experimental data (symbols) of the H<sub>2</sub>S/SO<sub>2</sub> conversion for gas streams containing 1.0% H<sub>2</sub>S, 0.5% SO<sub>2</sub>, and 0% to 30% H<sub>2</sub>O.

which influence the effective diffusivity. The catalyst size, on the other hand, affects the effectiveness factor, a rating factor for the diffusion effect ranging from 0 to 1, through a Thiele modulus. Increasing catalyst size will increase the Thiele modulus which, in turn, decreases the effectiveness factor. As a result, conversion efficiency of larger catalysts is not expected to be as high as that of smaller catalysts at extremely high space velocities where pore diffusion is a rate-limiting step. However, at low space velocities or high temperatures, the pore diffusion limitation becomes inconsequential because of thermodynamic equilibrium. In such a case, effectiveness factor becomes 1, and no size effect on conversion efficiency should be observed.

Based on the data presented above, the thermodynamic and kinetic regimes of the Claus reaction in packed beds can be defined. The GHSV-temperature space can be divided by a zone of transition into two regimes. The Claus reaction which is run at conditions above the transition zone is limited by kinetics. On the other hand, if the conditions are located below the transition, it certainly will be limited by thermodynamics. As temperature increases, the transition zone moves to higher GHSVs since the rate

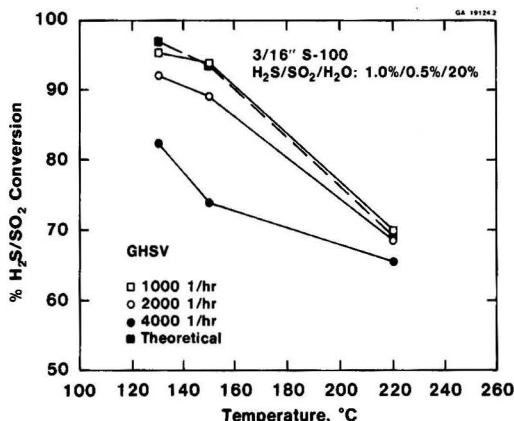


Figure 11. Effects of temperature on the H<sub>2</sub>S/SO<sub>2</sub> conversion efficiency of 3/16" S-100 Claus catalyst for gas stream containing 1.0% H<sub>2</sub>S, 0.5% SO<sub>2</sub>, and 20% H<sub>2</sub>O.

is also increased. However, the change is not extremely sensitive to temperature changes under the conditions studied. The width of the transition band increases slightly as temperature increases. This indicates that the change in reaction regimes becomes less sensitive to space velocity as temperature increases. Shown in Figure 9 is such a plot for 1/4- and 3/16-inch S-100. As one might expect, the transition zone for 3/16-inch catalyst is well above that of 1/4-inch catalyst. Therefore, the smaller the pellet sizes, the higher the transition zone in the GHSV-temperature chart. The zone for 1/8-inch S-100 would be expected to be only slightly higher than that for 3/16-inch S-100.

#### Effect of Water Vapor

The presence of water vapor in the acid gas has been known to cause the decline of sulfur conversion efficiency [11]. As one of the reaction products, the presence of a large amount of water vapor inevitably shifts equilibrium to the reactant side of the equation. The water effect is believed to be more significant at the third converter reaction where the  $H_2S$  concentration is lower. Figure 10 shows the effects of various amounts of water vapor on theoretical conversion efficiencies as predicted by the SOLGASMIX program. It shows that theoretical conversion efficiencies are significantly reduced by including 10% water vapor in the inlet gas stream. Further increasing water content to 20% and 30% continues to lower the efficiencies, but at a decreasing significance. Also, the water vapor greatly changes the temperature dependence of the equilibrium conversion. For example, the conversion efficiency for the reaction with 1%  $H_2S/0.5\%$   $SO_2$  drops about 20% when the temperature increases from 150°C to 350°C. But with an additional 20% water vapor involved, the equilibrium conversion loses as much as 95% for the same range of temperature increase.

The predicted efficiencies were found to be consistent with that measured. Although it was not attempted to verify the entire curves, the data obtained under certain conditions, as shown by symbols in Figure 10, do agree well with the predictions. The data at 130°C and 150°C were run under sub-dew point conditions and were collected before any significant amount of elemental sulfur was deposited on the catalyst.

Not only the presence of water vapor in the acid gas unfavorably shifts the equilibrium of the modified-Claus reaction, but it has also been reported to slow down the rate of approaching that equilibrium [12]. The retarding effect may be caused by the competitive adsorption of water vapor and sulfur species for active sites on the surface. Figure 11 shows conversion efficiency as a function of temperature for reaction with 1%  $H_2S/0.5\%$   $SO_2/20\%$   $H_2O$  and space velocities at 1000, 2000, and 4000 1/hr. For 1000 GHSV, the reaction did not seem to be retarded by the presence of water vapor and the theoretical efficiencies were achieved. Increasing GHSV to 4000 1/hr reduced the conversion quite significantly, indicating the slower kinetics. However, the slower kinetics may also be the result of the lower temperature. According to a rate equation proposed by Dalla Lana et al. [12], the presence of 20% water vapor will reduce the rate of  $H_2S/SO_2$  reaction by about 40%. However, decreasing temperature from 220°C to 130°C will reduce the rate of reaction by as much as five times. Therefore, though the slower kinetics caused by the presence of water vapor is real, its effect is secondary as compared with the effect of temperature. This statement is particularly true when the reaction temperature is so high that the intrinsic kinetics is no longer a controlling mechanism.

Based on the above justification, the definition of reaction regimes for the  $H_2S/SO_2$  reaction with water vapor

should not be significantly different from those defined in Figure 9, the one without water vapor. When the reaction temperature is lowered to below sulfur dew point, the corresponding GHSV that defines the transition zone should also be dropped to a much lower level.

#### CONCLUSIONS

This study shows that Alcoa S-100 catalyst is capable of converting  $H_2S/SO_2$  to the level predicted by thermodynamics under the three converter conditions and GHSV up to 2000. The measured data agree with the thermodynamic equilibrium conversion predicted by Alcoa's SOLGASMIX computer program, which gives total sulfur conversions of 89.5, 92.01 and 95.8% under first, second, and third converter conditions, respectively. Since most Claus plants are operated at GHSV less than 1000  $hr^{-1}$ , catalyst activity of S-100 is well above that required for a successful operation of Claus reactors.

As GHSV increases to 3000 and above, 1/4-inch S-100 catalyst performance gradually runs into the kinetic regime and the conversion efficiency declines. However, 3/16- and 1/8-inch S-100 catalysts are able to maintain their equilibrium conversions up to 6,000 GHSV for all three converter conditions. The fact that smaller catalysts yield higher conversion efficiencies, along with other reasons, leads to the conclusion that pore diffusion is the rate-controlling step in the kinetic regime. The improvement in performance is much more significant for 3/16-inch over 1/4-inch than for 1/8-inch over 3/16-inch.

Although it is unlikely for the Claus plant to operate at high GHSVs reported in this study, the conversion data at high GHSVs could be implicitly related to the conversion of aged catalysts at normal GHSVs. It is because fewer active sites available for reaction in aged catalysts is analogous to running the reactor with fresh catalysts at a higher GHSV. In addition to the loss of active sites, aging of catalysts might be associated with the collapse and plugging of the pores in catalysts. And this could lead to increased pore diffusion resistance. Therefore, smaller catalysts should provide longer service life. Since the pressure drop of a packed column increases with decreasing pellet size, the 3/16-inch S-100 catalyst should represent a better choice for industrial applications, where maximum activity is required. For reaction with pressure drop limitations, 1/4-inch S-100 is recommended.

#### ACKNOWLEDGMENT

The author wishes to thank Western Research for their consultation in developing the Claus unit and confirming the data.

#### LITERATURE CITED

1. Steijns, M. and P. Mars, "Catalytic Oxidation of Hydrogen Sulfide. Influence of Pore Structure and Chemical Composition of Various Porous Substances," *I&EC, Prod. Res. Dev.*, Vol. 16, No. 1, pp. 35-41 (1977).
2. George, Z. M. and R. W. Tower, "Catalytic Activity of Faujasite-Type Zeolites Towards the Claus Reaction," *Can. J. of Chem. Eng.*, Vol. 63 (Aug. 1985).
3. Gamson, B. W. and R. H. Elkins, "Sulfur from Hydrogen Sulfide," *Chem. Eng. Prog.*, Vol. 49, No. 4 (1953).
4. Pearson, J. M., "Recent Development in Claus Catalysts," paper presented at the Canadian Natural Gas Processor's Association in Calgary (Nov. 24 1972).
5. Goodboy, K. P., "How to Achieve Greater Sulfur Conversion Efficiencies," paper presented at the Petroenergy 83 (Sept. 15, 1983).

6. Goodboy, K. P., "Catalyst Increases COS Conversion," Oil and Gas Journal (Feb. 18, 1985).
7. Pearson, M. J., "Special Catalyst Improved C-S Compounds Conversion," Hydrocarbon Processing (April 1981).
8. McGregor, D. E., C. L. Liu, and I. G. Dalla Lana, "On-Line Measurement of Catalytic Reaction Rates," paper presented at 20th Canadian Chem. Eng. Conference, Sarnia (1970).
9. Carberry, J. J., Chemical and Catalytic Reaction Engineering, McGraw Hill (1976).
10. Alcoa Product Data, ChE 942, Form No. F35-14251 (April 1986).
11. Paskall, H. G., "Capacity of the Modified-Claus Process," published by Western Research, Calgary, Alberta, Canada (March 1979).
12. Dalla Lana, I. G., D. E. McGregor, C. L. Liu, and A. E. Cormode, "A Kinetic Study of the Catalytic Reaction of H<sub>2</sub>S

and SO<sub>2</sub> to Elemental Sulfur," Proc. 5th Europ./2nd Int. Symp. Chem. Reaction Eng., B2-9 (1972).



C.-L. (Joe) Chou is a Senior Engineer in the Chemical Systems Division of Alcoa Technical Center, specializing in heterogeneous reaction kinetics related to sulfur recovery, adsorption phenomena, and mathematical modeling. He received his B.S. degree from National Taiwan University (1974), M.S. degree from West Virginia University (1979), and Ph.D. from Carnegie-Mellon University (1983), all in Chemical Engineering. He has authored several technical papers in the area of adsorption and reaction kinetics, and is a registered professional engineer in the state of Pennsylvania.

# Controlling Acid Deposition by Seasonal Gas Substitution in Coal- and Oil-Fired Power Plants

Gary Galeucia, Dan Golomb, and James A. Fay

Massachusetts Institute of Technology, Cambridge, MA 02139

*Based on evidence that the rate of wet sulfate deposition in eastern North America is higher in the summer half of the year than in the winter half, seasonal control of emissions is proposed as a means of minimizing acid deposition control costs. This paper evaluates the proposal that natural gas be substituted for coal and oil in electric power plants during April through September. A model is presented that simulates the substitution of natural gas for coal and oil in power plants in the eastern 31 state region, so as to minimize total costs with respect to deposition reductions at an Adirondack receptor. The results of the model show: 1) the increased effectiveness of seasonal versus year-round controls; 2) changes in fuel consumption levels as a result of substitution; and 3) the costs of achieving various levels of deposition reduction at an Adirondack receptor. The costs of seasonal gas substitution are compared to cost estimates for other proposed control methods. The conclusion is that seasonal gas substitution is cost-competitive with other control methods, at least in some plants and states.*

Recently, several proposals have been advanced that move away from broad-based reduction of acid rain precursor emissions toward more efficient policies that recognize the *spatial relationship* between emission sources and the areas sensitive to the acid deposition caused by these emissions [1-4]. This paper proposes that acid rain policy should step beyond the spatial relationship toward a recognition of the *temporal relationship* between emissions and depositions; namely, that there are significant seasonal variations in deposition rates despite a relatively constant rate of emissions. Just as it is more efficient to exert greater control of emissions from sources that are relatively close to sensitive areas, it is also more efficient to impose greater control of emissions at times when the deposition rates are highest.

Recent work in atmospheric modeling has shown that differences in seasonal rates of sulfate deposition create the opportunity for seasonal control of sulfur emissions as a more efficient means of reducing annual amounts of sulfate deposition [4]. By electing to reduce SO<sub>2</sub> emissions in the summer half of the year, there would result a larger reduction of annual deposition per ton of SO<sub>2</sub> removed than if the same quantity were removed year-round. It may prove to be less expensive to reduce deposition by controlling emissions in the summer half of the year, rather than year-round.

To evaluate this new strategy, seasonal substitution of natural gas for coal and oil in electric utility boilers during April through September is investigated. A model is presented that simulates the substitution of natural gas for coal and oil so as to minimize the cost of achieving various deposition reductions. The model is static in that it simulates reductions for a single year: 1983. It uses the actual price and consumption of coal, oil, and gas for that year. The model is concerned with emissions of sulfur dioxide (SO<sub>2</sub>) from electric utilities in the 31 eastern states and the District of Columbia (D.C.) as well as the resulting wet deposition of sulfate (SO<sub>4</sub>) at a single receptor in the Adirondack Mountains of New York. The results of the model exercise show: 1) the increased effectiveness of seasonal versus annual sulfur emission reductions, and 2) the cost of seasonal gas substitution. The cost, in terms of emission and deposition reductions achieved, is compared to cost estimates for other proposed control methods and strategies. An example is given for calculating the cost of deposition reduction for a source oriented strategy, to which the cost of a receptor oriented strategy by seasonal gas substitution can be fairly compared. The conclusion of the cost comparison is that seasonal gas substitution is cost competitive with the year-round control strategies, at least for some plants in some states.

The model does not consider in depth two important

factors: 1) the availability of gas supply, and 2) the capital cost for seasonal gas substitution. These factors are discussed briefly, with the conclusions that there may be restrictive limits to gas supply and deliverability, and that capital costs for seasonal gas substitution are probably very low relative to control methods such as flue gas desulfurization.

### SEASONAL VARIATION IN DEPOSITION RATES

Analysis of several years of precipitation chemistry data has established that wet sulfate deposition rates in the northeastern U.S. and southeastern Canada are higher in the summer months (April-September) than in the winter months (October-March) [4-5]. Figure 1 shows the seasonal patterns of sulfate deposition over three years at four receptors. Seasonal differences in sulfate deposition are evident.

The exact causes of the differences in seasonal deposition patterns are not well understood; they are probably linked to the faster conversion rate in summer of the precursor  $\text{SO}_2$  emissions to the deposited  $\text{SO}_4$  (sulfate) and to the seasonal storm tracks. Raynor and Hayes [6] observed that sulfate (and hydrogen) ion concentrations are highest in precipitation associated with cold fronts and squall lines, which occur most frequently in the summer months. The quantity of sulfate being deposited in a storm is a function of the previous trajectory of the polluted warm, moist air mass and the amount of precipitation in the storm. In winter, more of the unoxidized  $\text{SO}_2$  is blown offshore and hence does not fall on the land as acid wet sulfate.

Although the chain of processes from emission of pollutants to eventual deposition of acid and acid-producing substances is complex and not fully understood, all evidence points to a linear relationship between emissions and deposition. Current scientific understanding indicates that reducing sulfur dioxide emissions would proportionally reduce the deposition of sulfate. The contribution of individual sources to the deposition at a given receptor may be estimated by means of atmospheric transport models.

### ATMOSPHERIC TRANSPORT MODEL

The seasonal gas substitution model utilizes an atmospheric transport model for determining deposition ef-

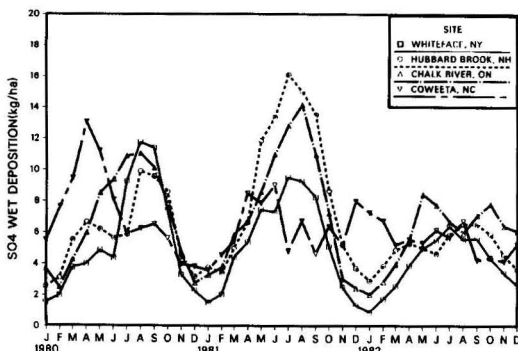


Figure 1. Seasonal patterns of wet sulfate deposition at four receptors in eastern North America. Three-monthly cumulative deposition ( $\text{kg SO}_4$  per hectare, per three months) plotted by middle month. Except in Coweeta, NC, 70 to 80% of the annual deposition occurs between April through September. In 1982, the annual wet deposition was low everywhere, but the seasonal pattern still is noticeable.

TABLE 1. SEASONAL TRANSFER COEFFICIENTS FOR ADIRONDACK RECEPTOR (kilograms sulfur per hectare wet-deposited per teragram sulfur emitted)

State	Winter	Summer
AL	0.2579	0.5908
AR	0.1742	0.3627
CT	0.7903	1.8720
DC	0.6007	1.6180
DE	0.6274	1.6360
FL	0.2300	0.4323
GA	0.2988	0.6938
IL	0.2805	0.7104
IN	0.3117	0.8085
IA	0.1852	0.4153
KY	0.3356	0.8671
LA	0.1650	0.3120
MA	0.7230	1.6480
MD	0.6287	1.6780
ME	0.5225	1.0410
MI	0.4045	1.0980
MN	0.1373	0.2772
MS	0.2068	0.4390
MO	0.2033	0.4641
NC	0.4397	1.1200
NH	0.8752	1.7890
NJ	0.7373	1.8810
NY	0.9127	2.1840
OH	0.4641	1.2940
PA	0.6339	1.7750
RI	0.7230	1.6480
SC	0.3486	0.8223
TN	0.3027	0.7463
VA	0.5310	1.4130
VT	1.2950	2.6180
WV	0.4979	1.3710
WI	0.2500	0.6106

Source: [8].

fects of emission reduction [4, 7]. The model is empirically based in that the model parameters are determined from comparison with wet deposition measurements. The acid deposition model provides transfer coefficients that define the quantity of deposition at a receptor per unit of emission at a source. Transfer coefficients have been obtained for both annual and seasonal (summer/winter) periods [8]. The seasonal gas substitution model uses the summer transfer coefficients to relate deposition reductions at an Adirondack receptor to emissions reductions resulting from natural gas substitution. Table 1 lists the values of the seasonal transfer coefficients between the 31 eastern states plus D.C. and an Adirondack receptor. Table 1 shows that the summer transfer coefficients are about 2 to 3 times as large as the winter ones. In other words, summer emissions from the 31 eastern states cause nearly 2 to 3 times the deposition at an Adirondack receptor as an equal quantity of winter emissions.

Because the transfer coefficient  $T_{ij}$  is the ratio of the amount of deposition at receptor  $j$  contributed by source  $i$  divided by the emission amount from source  $i$ , the total deposition  $D_j$  at receptor  $j$  equals the sum of the products of the transfer coefficient  $T_{ij}$  times the emission  $Q_i$ :

$$D_j = \sum_i T_{ij} Q_i \quad (1)$$

When seasonal transfer coefficients are used, the annual (A) deposition is obtained by summing separately the products of the seasonal transfer coefficients  $T_{ij}$  and emissions  $Q_i$  for summer (S) April-September and winter (W) October-March:

$$(D_i)_A = \left( \sum_i T_{if}Q_i \right)_s + \left( \sum_i T_{if}Q_i \right)_w \quad (2)$$

By selecting a desired annual deposition quantity, the allowable level of emissions may be determined, which in turn determines the amount of gas substitution necessary to reach the reduced emission levels.

**SO<sub>2</sub> Emissions:** Most legislative proposals to date have focused on a 31 state region encompassing the states east of, and bordering on, the Mississippi River. Of the 26 to 27 million tons\* of sulfur dioxide emitted in the continental United States in 1980, about 22 million tons came from the 31 state region [10]. Table 2 lists 1983 emissions of SO<sub>2</sub> attributable to the burning of coal and residual oil in electric power plant boilers in the 31 eastern states and D.C. The electric utilities included in this analysis are estimated to have contributed 16 million tons of SO<sub>2</sub> emissions in 1983. Emissions were calculated from annual electric utility coal and oil consumption data [9], neglecting any sulfur removal processes that have been used in that year. These emissions are used by the model for calculating deposition reductions at an Adirondack receptor.

Since sulfur emission rates in most states are fairly constant throughout the year [10], the model assumes that fuel consumption during April through September is equal to one-half of the annual fuel consumption.

TABLE 2. ANNUAL SULFUR EMISSIONS FROM COAL- AND OIL-FIRED POWER PLANTS IN THE 31 EASTERN STATES AND D.C., 1983

State	Million Tons SO <sub>2</sub>		
	Coal	Oil	Total
AL	0.536	0	0.536
AR	0.070	0	0.070
CT	0	0.054	0.054
DC	0	0.001	0.001
DE	0.060	0.016	0.076
FL	0.458	0.213	0.671
GA	0.843	0	0.843
IA	0.197	0	0.197
IL	1.210	0.010	1.220
IN	1.534	0	1.534
KY	1.225	0	1.225
LA	0.032	0	0.032
MA	0.077	0.149	0.226
MD	0.197	0.015	0.212
ME	0	0.011	0.011
MI	0.606	0.001	0.607
MN	0.157	0	0.157
MO	1.218	0.002	1.220
MS	0.091	0	0.091
NC	0.367	0	0.367
NH	0.512	0.017	0.068
NJ	0.088	0.016	0.104
NY	0.230	0.229	0.460
OH	2.071	0	2.071
PA	1.583	0.033	1.616
RI	0	0.002	0.002
SC	0.182	0	0.182
TN	0.674	0	0.674
VA	0.123	0.006	0.130
WI	0.456	0	0.456
WY	1.007	0	1.007
TOTAL	15.346	0.777	16.123

Calculated from [9].

\*Tons are reported here in English units. 1 short ton = 0.907 tons metric.

TABLE 3. SUMMER AND ANNUAL SULFUR DEPOSITION CONTRIBUTED BY POWER PLANTS IN THE 31 EASTERN STATES AND D.C. IN 1983 (kilograms sulfur per hectare per year)

State	Summer Deposition		Annual Deposition	
	Coal	Oil	Coal	Oil
AL	0.071	0	0.098	0
AR	0.006	0	0.008	0
CT	0	0.023	0	0.029
DC	0	0.001	0	0.001
DE	0.022	0.006	0.028	0.007
FL	0.044	0.021	0.068	0.032
GA	0.132	0	0.179	0
IA	0.018	0	0.026	0
IL	0.193	0.001	0.256	0.002
IN	0.279	0	0.362	0
KY	0.239	0	0.309	0
LA	0.002	0	0.003	0
MA	0.029	0.055	0.038	0.073
MD	0.074	0.006	0.091	0.007
ME	0	0.003	0	0.004
MI	0.150	0	0.188	0
MN	0.010	0	0.015	0
MO	0.127	0	0.178	0
MS	0.009	0	0.012	0
NC	0.092	0	0.119	0
NH	0.021	0.007	0.028	0.009
NJ	0.037	0.007	0.046	0.008
NY	0.113	0.113	0.141	0.141
OH	0.603	0	0.738	0
PA	0.632	0.013	0.756	0.016
RI	0	0.001	0	0.001
SC	0.034	0	0.045	0
TN	0.113	0	0.150	0
VA	0.039	0.002	0.049	0.003
WI	0.063	0	0.085	0
WV	0.311	0	0.381	0
TOTALS	3.464	0.258	4.401	0.333

**Wet Sulfate Deposition:** The amount of wet sulfate deposition at a receptor can be linearly related to the amount of sulfur emissions from sources as in Eq. (2). Total 1980 annual wet sulfate deposition from all U.S. and Canada sulfur sources at an Adirondack receptor was estimated to be 27.5 kilograms sulfate per hectare per year (kg SO<sub>4</sub> ha<sup>-1</sup>y<sup>-1</sup>) [7]. Table 3 contains the 1983 summer and annual deposition amounts at an Adirondack receptor calculated to have been contributed by the sources included in this analysis. (Note: It is necessary to multiply the figures in Table 3 by a factor of three in order to convert sulfur (S) to sulfate (SO<sub>4</sub>). SO<sub>4</sub> is three times the molecular weight of S.) We calculate that electric utilities in the eastern 31 states in 1983 contributed 14.2 kg SO<sub>4</sub> ha<sup>-1</sup> to an Adirondack receptor, or 52% of the 1980 base amount. Of the 14.2 kg annual total, about 80% is calculated to be deposited between April and October. Summer deposition is disproportionately higher because the summer transfer coefficients are much larger than the winter ones (see Table 1).

#### WHY NATURAL GAS?

Annual depositions can be reduced more easily by substituting lower sulfur fuels for higher sulfur fuels during periods with higher deposition rates. This paper evaluates the annual wet sulfate deposition reduction that would result from substituting natural gas for coal and residual oil in utility boilers during the "summer" season, April through September.

Natural gas was chosen as a substitute fuel because it produces virtually no sulfur dioxide and can be readily burned in most oil- or coal-fired boilers. Seasonal gas sub-

stitution allows a continued utilization of existing coal resources in the winter half of the year, while requiring increased utilization of natural gas during the summer half of the year.

Important factors to be considered in seasonal natural gas substitution strategies include:

1. In the summer months there is currently excess capacity in the natural gas distribution system. According to Wilkinson [11], only 78% of the pipeline capacity is used in the summer months, and in some regions as little as 51%. (Summer gas supply and deliverability will be discussed later in this paper.)

2. Seasonal gas substitution could be implemented rapidly relative to the period needed to install flue gas desulfurization systems or develop new "clean burning" technology for a large number of plants. A quick implementation schedule would allay fears that further delays in reducing acid deposition might cause irreparable damage to the environment.

Additional benefits, beyond lower sulfate deposition, from seasonal gas substitution include:

1. Improved local air quality with lower ambient air concentrations of SO<sub>2</sub> and particulates during the summer months, when the highest levels usually are encountered.

2. Improved summertime visibility.

3. Increased potential for achieving attainment of air quality standards for SO<sub>2</sub> in non-attainment areas.

4. Decreased dependence upon imported oil.

5. Reduced sensitivity to fuel supply disruptions, e.g., coal strikes or oil embargos.

6. Increased reliance on domestic energy resources.

7. Decreased land requirements and cost for scrubber sludge and flyash disposal.

Natural gas has never been a favored utility boiler fuel in most parts of the eastern U.S., accounting for only about 10% of the total fuel heat consumed by electric utilities in the eastern 31 states [12]. The primary reason for this pattern of usage is that natural gas is a more expensive boiler fuel than is coal. This reason is certainly a viable one. There are two less viable reasons why natural gas may continue to be disfavored as a boiler fuel. The first concerns the perception that gas reserves are imminently exhaustible; the second is that gas use in utilities is legally constrained.

A reasonable estimate for the amount of the remaining conventional natural gas in the lower 48 of the United States that is recoverable under present and easily foreseeable technological and economic conditions is 12 to 25 × 10<sup>12</sup> m<sup>3</sup> (430 to 900 trillion cubic feet [Tcf]), as of December 1982 [12]. (This resource estimate does not include Alaskan, Canadian, Mexican, or unconventional resources.) At a consumption rate of 20 Tcf per year, slightly higher than present consumption, the resource estimated above will last 21 to 45 years. One explanation for the perception of imminent exhaustibility is that in the 1970s, gas demand exceeded gas supply as a result of price controls on natural gas. The market disequilibrium created the image that we are running out of gas.

The perception of imminent exhaustibility led policymakers to restrict gas use, which in turn has created the second misconception, namely that gas use is restricted. Restrictions on gas use in electric utility power plants were enacted when the federal Powerplant and Industrial Fuel Use Act (PIFUA) of 1978 was signed into law on November 9, 1978. However, PIFUA restrictions were sharply repealed by the Omnibus Budget Reconciliation Act signed into law on August 13, 1981. Since the 1981 amendment, PIFUA restrictions on natural gas use do not apply to "existing" power plants at all. A power plant is "existing" if it was in service or under construction prior to November 9, 1978 [13]. Furthermore, exemptions are available to post-1978 power plants. Pre-1978 power

plants contribute the bulk of total SO<sub>2</sub> emissions because 1) most generating units were built prior to 1978, and 2) older plants are subject to less restrictive pollution control regulations.\*

## THE SEASONAL GAS SUBSTITUTION MODEL

A model for evaluating the effects of seasonal gas substitution includes components for calculating sulfur emissions reductions, wet sulfate deposition reductions, changes in fuel consumption, and incremental expenditures for fuel purchases. The model's SO<sub>2</sub> emission sources are 376 utility plants burning coal or residual oil as a primary boiler fuel in the eastern 31 states and Washington, D.C. The criteria for including a plant in the model are that it have a rated capacity of 50 megawatts or larger, and at least 10% of the total heat has to be generated from either coal or oil. A complete description of the model, including the list of the 376 power plants and their fuel usage, is given by Galeucia [14]. Here we briefly summarize the model and its results.

The seasonal gas substitution model is a linear program (LP) that seeks to minimize the incremental spending on fuel purchases when natural gas is substituted for coal or oil. For each electric power plant *i*, there is a cost differential between a given heat content of gas and coal or gas and oil. Multiplying this cost differential by the quantity of heat required gives the incremental spending on fuel purchases by the power plant.

Minimization of the incremental spending for natural gas substitution is performed subject to two constraints. The first specifies the desired level of deposition, as has already been described above by Eq. (2). The second constraint requires that the same fuel heat value is consumed by each power plant under the gas substitution strategy as was actually required when no substitution occurred. The heat consumption of each source is equal to the heat content multiplied by the quantity of coal, oil, or gas consumed. Actual heat output was determined from fuel heat content and consumption data [9].

The LP model in its functional form seeks to minimize the sum of the products:

$$\text{MIN } \sum_i F_i G_i H^* \quad (3)$$

subject to:

$$D_A = \left( \sum_i T_{ij} Q_i \right)_s + \left( \sum_i T_{ij} Q_i \right)_w \quad (4)$$

$$G_i H^* = C_i H^c + O_i H^o \quad (5)$$

where the symbols are:

- C<sub>*i*</sub> = quantity of coal displaced at power plant *i*
- D<sub>A</sub> = annual target seasonal deposition quantity for a specified receptor
- F<sub>*i*</sub> = fuel cost differential between gas and coal or gas and oil per unit of heating value
- G<sub>*i*</sub> = quantity of natural gas substituted seasonally for coal or oil
- H<sup>c</sup> = unit heating value of coal
- H<sup>\*</sup> = unit heating value of natural gas
- H<sup>o</sup> = unit heating value of oil
- O<sub>*i*</sub> = quantity of oil displaced

The Adirondacks receptor is used in the model because it is environmentally sensitive and centrally located with respect to other environmentally sensitive areas in the U.S. and Canada. By adding additional deposition constraints, the model could be made to consider more than

\*Note added in proof: In 1987, Congress amended PIFUA. Public Law 100-42 essentially removes all legal constraints on gas use in existing utility boilers and industrial facilities.

one receptor. This would require the use of a set of transfer coefficients for each additional receptor. For simplicity of presentation, the model has been limited to a single receptor.

#### CALCULATING THE COST OF SEASONAL GAS SUBSTITUTION

Incremental spending on fuel purchases of natural gas by utilities is assumed to equal the product of the incremental quantity of natural gas consumed at a power plant as a result of substitution, the gas fuel heating value, and the cost differential per unit of heating value between gas and coal, or gas and oil, summed for all power plants (Eq. 3). It should be noted that the costs derived here for seasonal gas substitution are solely the result of the fuel price differentials between gas and coal or oil. Preliminary estimates of the incremental capital and operating costs associated with seasonal gas substitution indicate that the fuel price differential is by far the major cost.

The coal and oil prices used in the analysis are actual average prices per unit heating value paid by each power plant in 1983 [9]. The gas prices used are the state-average price paid by electric utilities in that state (Table 4). If no electric utility burned gas in a state, then the average price paid by industrial consumers was used [15]. From the gas prices listed in Table 4, it can be seen that prices vary significantly from state to state. The actual coal and oil prices, as well as the state-average gas prices, are not necessarily indicative of current and future prices, and therefore of price differentials, for these fuels. A fall in oil prices, which are dependent on the world market, could be expected to produce a decrease in natural gas

TABLE 4. AVERAGE COST OF NATURAL GAS AT ELECTRIC UTILITIES IN THE 31 EASTERN STATES AND D.C., 1983\$

State	\$/10 <sup>6</sup> Btu
AL	3.129
AR	3.211
CT	5.930(b)
DE	4.180
DC	4.480(a)
FL	2.529
GA	4.177
IL	5.291
IN	4.238
IA	3.747
KY	4.551
LA	3.150
MA	3.887
MD	4.480(a)
ME	7.660(b)
MI	4.388
MN	3.798
MS	3.325
MO	4.164
NC	4.860(a)
NH	6.000
NJ	4.046
NY	3.932
OH	5.169
PA	5.104
RI	3.753
SC	4.285
TN	3.870(a)
VT	4.220(a)
VA	4.202
WI	4.284
WV	4.546

(a) Average prices calculated from data reported on Form EIA-176.

(b) Average 1983 price paid by industrial consumers.

Sources: [9, 15].

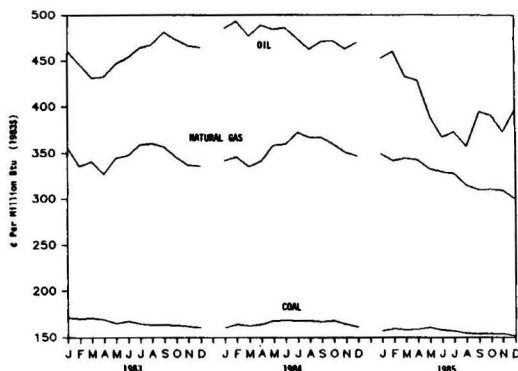


Figure 2. Average cost of fuel at U.S. electric power plants in 1983-85 (1 Btu = 1,055 kJ).

prices because the two fuels are to some extent interchangeable. Coal prices are affected to a greater extent by production costs, and to a lesser extent by the prices of oil and gas because these fuels are not close substitutes. Hence, a fall in oil prices and a subsequent fall in gas prices should be accompanied by a relatively smaller decrease in coal prices. The result is that in a period of lower oil prices, a smaller price differential between gas and coal could be expected.

To test this hypothesis informally, it is useful to look at gas, coal, and oil prices and price differentials over time (Figure 2). Prices were adjusted to 1983 dollars using the U.S. Bureau of Labor Statistics producer index for crude energy materials. During the period 1983 to 1985, the price of oil rose fairly steadily throughout 1983 and into mid-1984, and then declined during the remainder of 1984 and throughout 1985. The price of gas followed a similar pattern to that of oil, but the rise and fall are less pronounced. The price of coal remained relatively stable throughout the period. The historic prices are used here as a first approximation and illustration of the fuel price differential trends in current years. A more detailed analysis should include forecasts of fuel prices and consider the increased demand for gas.

#### MODEL RESULTS

The model is exercised by selecting various target levels of deposition reduction. The model selects a power plant to use seasonal gas substitution based on: 1) its share of the deposition, and 2) the fuel price differential. The share of deposition is a function of the sulfur content of the fuel and the transfer coefficient between the power plant and the receptor. Power plants that have relatively large transfer coefficients and small price differentials will be selected first.

The target level of deposition was reduced in 5% decrements of the base value of 27.5 kg ha<sup>-1</sup>y<sup>-1</sup> at an Adirondack receptor [7]. Corresponding levels of emissions reductions, gas substitution, coal and oil displacement, and resultant costs are calculated for each 5% decrement. These results are summarized in Table 5. For example, in the case of a 30% sulfate deposition reduction, 41 × 10<sup>9</sup> m<sup>3</sup> (1440 billion cubic feet [Bcf]) of natural gas are substituted in the summer half-year for 97 million tons of coal and 94 million barrels of oil at a cost of \$5.858 billion (1983\$). The resulting emission reduction would be 4.8 million tons of SO<sub>2</sub> per year.

The cumulative cost versus deposition reduction curve is shown in Figure 3. Cost is initially negative because there is a negative price differential between gas and oil at some plants.\* Since the objective is to minimize cost,



TABLE 5. RESULTS OF SEASONAL GAS SUBSTITUTION MODEL

Dep. Red. <sup>(a)</sup> (%)	Em. Red. (10 <sup>6</sup> tons SO <sub>2</sub> )	Gas Subst. Bcf	Coal Displaced (10 <sup>6</sup> tons)	Oil Disp. (10 <sup>6</sup> bbl)	Total Cost (10 <sup>9</sup> 1983\$)
5	0.6	337	8	79	-.204
10	1.3	501	20	84	.610
15	2.2	709	37	87	1.671
20	2.9	909	53	87	2.929
25	3.9	1179	76	87	4.403
30	4.8	1440	97	94	5.858
35	5.9	1795	127	95	7.867
40	6.9	2396	176	97	10.931

<sup>a</sup>Based on 27.5 kg ha<sup>-1</sup>y<sup>-1</sup> total deposition of wet sulfate at an Adirondack receptor.

the seasonal gas substitution model chooses the plants with negative price differentials first. As larger decrements of deposition are sought, the model selects plants with ever smaller shares of deposition and ever larger fuel price differentials. At the 40% deposition decrement, virtually all power plants in the eastern United States would have to convert to summer gas substitution with an attendant annual fuel price differential of nearly \$11 billion. Clearly, gas substitution ceases to be a preferred mode beyond a point where year-round emission control by fuel substitution (e.g., low-sulfur coal) or flue gas desulfurization becomes more cost effective. An overall optimized (least-cost) deposition-oriented control strategy would have to consider a plant-by-plant costing of emission control options. The options ought to include the whole range of emission controls, from summer gas substitution to year-round flue gas desulfurization.

#### COMPARISON WITH ALTERNATIVE DEPOSITION REDUCTION SCHEMES

The debate over alternative strategies for controlling acid rain has focused mainly on the expected costs of

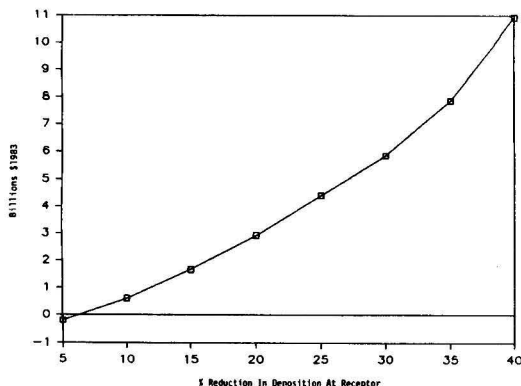


Figure 3. Cumulative cost curve for deposition reductions at Adirondack receptor. Deposition decrements achieved by summer gas substitution at eastern U.S. power plants. Calculations based on estimated total deposition from all U.S. and Canadian sources of 27.5 kg SO<sub>2</sub> ha<sup>-1</sup> y<sup>-1</sup>.

\*This condition raises the question of why these plants do not convert from oil to gas regardless of pollution concerns. Indeed, some oil-fired plants practice summer gas substitution purely on economic grounds, e.g. Boston Edison's Mystic Unit #7. We have not investigated why this practice is not in wider use. Existing long-term contracts and the availability of gas supply may play a role.

reducing SO<sub>2</sub> emissions. Total cost and \$/ton of SO<sub>2</sub> removed are frequently used to compare alternative control strategies. In making these comparisons, a distinction should be made between source-oriented strategies aimed solely at reducing total emissions and receptor-oriented (or targeted) strategies that maximize the amount of deposition reduction at a receptor(s) for a unit of emission reduction. A direct comparison of the cost of receptor- and source-oriented strategies can be misleading; these strategies will not result in equal deposition reductions at a given receptor for equal emission reductions.

Morrison and Rubin [16] developed a model that computes the emission reduction and cost that would result from coal-fired utility plant emission caps of 1.5 and 1.2 lb. SO<sub>2</sub> per million Btu (0.68 and 0.54 kg SO<sub>2</sub> per gigajoules, respectively) using optimized combinations of switching to lower sulfur coal and flue gas desulfurization (FGD). The 1.5 and 1.2 lb. emission caps would result in annual emission reductions of 8 and 10 million tons SO<sub>2</sub> respectively. Based on the distribution of emission reductions across the eastern 31 states and the model transfer coefficients, these emission reductions would respectively yield 7.2 and 8.2 kg SO<sub>2</sub> ha<sup>-1</sup>y<sup>-1</sup> deposition reductions at an Adirondack receptor, or 25% and 30% of the base value, respectively. Morrison and Rubin's calculated total cost ranges from \$1.5-2.6 and 3.2-4.7 billion (1980\$) for the 8 and 10 million tons emission reductions, respectively. Using a GNP deflator of 1.2 to adjust to 1983 dollars makes the cost range \$1.8-3.1 and \$3.8-5.6 billion, respectively. Using summer gas substitution in oil- and coal-fired power plants so as to equal the deposition reduction of the 8 and 10 million tons SO<sub>2</sub> scenario, the total cost would be \$4.4 and \$5.8 billion (1983\$), respectively (see Table 5). Despite the higher overall costs of seasonal gas substitution, there are individual plants where seasonal gas use will provide cheaper sulfur deposition reduction than FGD.

#### GAS SUPPLY FOR SUBSTITUTION

The seasonal gas substitution model has not considered gas deliverability constraints which may limit the amount of substitution that occurs within a state as specified by the model. A gas deliverability constraint would occur whenever the gas supply infrastructure lacks the necessary capacity to meet the incremental demand imposed by a level of gas substitution, or if total gas production is insufficient. In order to utilize gas substitution, the utility must access its gas supply from a gas distribution company's or gas transmission company's high-pressure pipeline. Transmission capacity can be expanded, but this may increase costs and make gas substitution less competitive relative to other control strategies.

Because the primary use of natural gas is for space heating, summer demand is lower than winter demand in nearly all states. This condition favors seasonal gas substitution, but not in an unlimited or universal pattern. The ratio of summer sales volume to winter sales volume averaged 49% and ranged from 33% to 103% in the 31 eastern states and D.C. in 1984 (Table 6). The winter/summer sales ratio is only an indicator of general capacity and cannot be relied upon as a definitive measure of excess capacity available to every generating unit within a state. If it is assumed that the difference between winter and summer consumption is an approximate measure of available capacity, the aggregate difference between summer and winter volume is 2050 Bcf, which could provide approximately enough gas substitution for a 37% reduction in deposition (from Table 5). However, not every state has the necessary surplus summer gas required at all levels of deposition reduction. For example, for a 25% deposition reduction, only 14 states have the surplus needed to supply their share of the model's solution (Table 7).

#### OTHER COSTS

Preliminary findings concerning incremental capital and operating costs for seasonal gas substitution reveal

TABLE 6. NATURAL GAS DELIVERIES TO RESIDENTIAL, COMMERCIAL, AND ELECTRIC UTILITY CONSUMERS IN THE 31 EASTERN STATES AND D.C.

State	Summer Volume <sup>a</sup> (Bcf)	Winter Volume <sup>b</sup> (Bcf)	Summer Volume as a Percent of Winter Volume
AL	21.9	55.4	40
AR	37.9	68.7	55
CT	20.2	39.8	51
DE	8.1	9.5	85
DC	9.7	20.9	48
FL	112.4	109.1	103
GA	43.8	107.9	41
IL	202.5	510.5	40
IN	65.6	173.0	38
IA	35.6	96.6	37
KY	28.5	78.4	36
LA	233.7	234.7	95
ME	0.5	1.1	45
MD	33.6	71.9	47
MA	73.8	115.1	64
MI	152.3	370.0	41
MN	46.6	134.3	35
MS	49.8	59.6	84
MO	51.3	137.0	37
NH	2.7	6.1	44
NJ	129.3	208.6	62
NY	256.1	410.5	62
NC	18.2	47.2	39
OH	141.1	377.6	37
PA	111.4	282.2	39
RI	10.1	16.1	62
SC	10.6	25.7	41
TN	21.1	63.5	33
VT	0.9	2.2	42
VA	24.1	51.5	47
WY	16.1	43.2	37
WI	48.1	119.1	40
TOTALS	2007.6	4057.6	49

(a) Summer—April through September; and (b) Winter—October through March.

NOTE: Industrial gas consumption is not included here as the data are not yet reported by the Energy Information Administration. Exclusion of this component probably causes the ratio of summer-to-winter volume to be slightly overstated here.

two significant points. First, capital costs are low and implementation is quick. Using as an example the Boston Edison Mystic #7 unit, an oil-fired generating unit that converted to seasonal gas use, the boiler modification and gas supply construction cost \$3.5 million for the 565 MW unit. The modification was completed in less than one year [17]. This is approximately \$6/kW. In contrast, capital costs for limestone flue gas desulfurization (scrubbing) are between \$175 and \$317/kW [18], and have much longer lead times. Second, ash generation is reduced. If the variable component of ash disposal is significant, there is a potential cost saving from seasonal gas substitution. For example, if bottom and flyash variable disposal costs are \$10/ton, a typical coal-fired power plant ash disposal cost would be \$2.6/kW annually. Seasonal gas substitution could save one-half of this sum. The present value of these savings are close to or may exceed the capital costs associated with seasonal gas substitution.

The crucial determinant of the cost-competitiveness of gas substitution is the price differential between gas and coal and gas and oil. Since long term prices are impossible to predict with certainty, gas substitution is regarded as being financially risky when compared with other control methods. Actually, gas substitution may be less risky than more capital intensive control methods. Because there is a relatively small capital investment associated with gas substitution, a utility could easily abandon it if a more cost-effective solution became available, without forfeiting a large investment. Because of the large capital outlay needed for scrubbing equipment, a utility saddled with an expensive scrubber is financially limited if it wants to exploit less expensive control methods that may become available.

#### CONCLUSIONS

Nearly all of the "acid rain" policy and policy analyses have focused on emission reductions and the cost of con-

TABLE 7. NATURAL GAS SUBSTITUTED FOR A 25% DEPOSITION REDUCTION

State	Gas (Bcf)	Sufficient Surplus (a)
AL	51	N
DC	1	Y
DE	19	N
FL	144	N
IA	3	Y
IL	20	Y
IN	73	Y
KY	61	N
MA	59	N
MD	40	N
MI	50	Y
MO	25	Y
MS	9	Y
NH	11	N
NJ	30	Y
NY	137	Y
OH	143	Y
PA	184	N
RI	1	Y
TN	41	Y
VA	3	Y
WI	2	Y
WV	68	N

1176

(a) The difference between winter and summer volume of sales is used as an approximate measure of summer capacity. If the difference between winter and summer sales (see Table 6) is greater than the incremental demand shown above, then Y.

trolling emissions. But it is deposition, not emissions per se, that matters. Monitoring has shown that deposition rates are significantly higher during April through September than during October through March despite equal emission rates. Based on this evidence, it is more efficient to control emissions (and hence deposition) during the summer half of the year. The cost-effectiveness of any control method should be related to its effect on deposition rather than its effect on emissions. One ton of SO<sub>2</sub> removed in the summer half of the year has a greater effect on deposition than reducing that ton year-round. We find that in terms of equal deposition reductions in the Adirondacks, the costs of seasonal gas substitution may be comparable to year-round controls in some plants and states.

Seasonal substitution of gas for coal or oil is a reasonable option for some utilities to control sulfate deposition. However, it is not a panacea for solving the acid rain problem. The quantities of gas needed for substitution in order to make total deposition reductions of more than a few kilograms per hectare would exceed existing gas supply in many states. Some generating units are located too far from a gas supply or face fuel cost differentials that are too large to make gas substitution economically competitive with other control methods. An overall optimized, least-cost, receptor-oriented strategy probably will include a mix of year-round emission controls and seasonal gas substitution.

#### ACKNOWLEDGMENT

This research was performed at the MIT Energy Laboratory with the support of the Electric Utility Program.

#### LITERATURE CITED

- Fay, J. A., D. Golomb, and J. Gruhl, "Controlling Acid Rain," Energy Laboratory, Report No. MIT-EL 83-004, Massachusetts Institute of Technology, Cambridge, MA 02139 (1983).
- Streets, D. G., "Opportunities for Improving the Cost-Effectiveness of Acid Rain Control Strategies," *Environmental Progress*, **5**, 82 (1986).
- Young, J. W. S. and R. W. Shaw, "Proposed Strategies for Reducing Sulfate Deposition in North America," *Atmospheric Environment*, **20**, 189 (1986).
- Golomb, D., J. A. Fay, and S. Kumar, "Seasonal, Episodic, and Targeted Control of Sulfate Deposition," *J. Air Poll. Control Assoc.*, **36**, 789 (1986).
- Bowersox, V. C. and G. J. Stensland, "Seasonal Variations in the Chemistry of Precipitation in the United States," Paper 85-6A.2 presented at the 78th Annual Meeting of the Air Pollution Control Association, Detroit, MI (1985).
- Raynor, G. S. and J. V. Hayes, "Concentrations of Some Ionic Species in Long Island, NY Precipitation in Relation to Meteorological Variables," *Water, Air, and Soil Pollution*, **17**, 309 (1982).
- Fay, J. A., D. Golomb, and S. Kumar, "Source Apportionment of Wet Sulfate Deposition in Eastern North America," *Atmospheric Environment*, **19**, 1773 (1984).
- Kumar, S., "Modeling Acid Deposition in Eastern North America," Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts (1985).
- Energy Information Administration, U.S. Department of Energy, "Cost and Quality of Fuels for Electric Utility Plants 1983," U.S. Government Printing Office, Washington, D.C. (1984).
- National Acid Precipitation Program, "Historic Emissions of Sulfur and Nitrogen Oxides in the U.S. from 1900 to 1980," EPA-600/7-85-009a, Washington, D.C. (1985).
- Wilkinson, P., "Seasonal Fuel Switching to Natural Gas: A Logical Approach to Reduce Sulfur Dioxide," *Gas Energy Review*, **12**, 11 (1984).
- Office of Technology Assessment, "U.S. Natural Gas Availability: Gas Supply Through the Year 2000," OTA-E-245, Congress of the United States, Washington, D.C. (1985).
- Bardin, D. J., "Real and Imagined Restrictions on Electric Utility Fuel Use of Natural Gas," *Public Utilities Fortnightly*, **115**, 27 (1985).
- Galeucia, G., "Controlling Acid Deposition by Seasonal Gas Substitution in Coal- and Oil-Fired Power Plants," Energy Laboratory Report No. MIT-EL 86-004, Massachusetts Institute of Technology, Cambridge, MA 02139 (1986).
- Energy Information Administration, U.S. Department of Energy, *Natural Gas Monthly*, Washington, D.C. (1984).
- Morrison, M. B. and E. S. Rubin, "Linear Programming Model for Acid Rain Policy Analysis," *J. Air. Poll. Control Assoc.*, **35**, 11 (1985).
- Kingston, P., personal communication, Boston Edison Company (1985).
- Miller, M. J., "Retrofit SO<sub>2</sub> and NO<sub>x</sub> Control Technologies for Coal-Fired Power Plants," Paper 85-1A.2 presented at the 78th Annual Meeting of the Air Pollution Control Association, Detroit, MI (1985).

**Gary Galeucia** is presently employed at Conoco, Inc. in Wilmington, Delaware. He was a Research Assistant at the MIT Energy Laboratory and earned his M.Sc. degree at the Sloan School of Management.

**Dan Golomb** is a Research Scientist at the Energy Laboratory and received his M.Sc. and Ph.D. degrees at the Hebrew University, Jerusalem. Before joining the Energy Laboratory, he was with the Environmental Protection Agency and the Air Force Cambridge Research Laboratory.

**James A. Fay** is Professor of Mechanical Engineering and serves as Director, Environmental Programs, at the Energy Laboratory. He received an M.Sc. degree from MIT and a Ph.D. degree from Cornell University.

# Fluid Flow and Gas Absorption in an Ejector Venturi Scrubber

Iclal Atay, Gordon Lewandowski, and Richard Trattner

Department of Chemical Engineering, Chemistry, and Environmental Science, New Jersey Institute of Technology, Newark, NJ 07102

*Empirical models were developed to describe the fluid flow characteristics and gas absorption efficiency of an ejector venturi scrubber. The empirical constants were determined experimentally using stop action photographs of the spray, static pressure measurements, and sulfur dioxide absorption efficiencies.*

*Experiments were conducted on a commercial scrubber, 24 inches (61 cm) high, with a 4 inch (10 cm) diameter gas inlet and outlet. Liquid flow rates varied from 3 to 8 gallons/min (.0114 to .0303 m<sup>3</sup>/min) in the atomizing range of the scrubber, and gas flows from 24 to 64 cubic feet/min (.680 to 1.81 m<sup>3</sup>/min).*

*The liquid-to-gas ratio was constant at .0167.*

*Droplet sizes ranged from 34 to 563 microns, with a volume mean diameter of 155 microns, at a liquid rate of 6 gpm (.0227 m<sup>3</sup>/min).*

*The sulfur dioxide mass transfer coefficient varied from 25 to 800 lb-mole/hr-ft<sup>3</sup> (400 to 12,800 kg-mole/hr-m<sup>3</sup>).*

## INTRODUCTION

The ejector venturi scrubber utilizes a high velocity liquid spray to pump the gas and remove objectionable components. The process relies on the transfer of kinetic energy from the liquid to the gas, and there is no blower in the system. The total energy requirement of the scrubber is accounted for by the liquid pump.

A schematic of the commercial scrubber used in the present study is shown in Figure 1. The scrubber height is 24 inches (61 cm), the gas inlet and diffuser outlet are 4 inches (10 cm) in diameter, and the throat has a 2 inch (5 cm) diameter. The length of the throat is 1 inch (2.5 cm), and of the diffuser section is 14-1/4 inches (36 cm) with a 5° taper.

The ejector venturi scrubber provides a higher interfacial area (due to finer droplet size) compared to the more common high energy venturi scrubber (in which a blower is used to move the gas). The ejector scrubber also has no obstructions to flow on the gas side, which can be a considerable advantage where sudden releases of gas can occur from upstream reactors and safety is a consideration. The higher liquid flow in an ejector scrubber also reduces scale formation, and effectively moderates the gas temperature.

## LITERATURE REVIEW

### Drop Size Distribution

The following phenomena have been postulated to play a role in the atomization of liquid jets (in addition to the physical properties of the fluids, nozzle geometry, and operating conditions):

- (1) Aerodynamic interaction between the liquid and gas phases [1].
- (2) Liquid turbulence [2].
- (3) Liquid cavitation [3].
- (4) Velocity profile rearrangement [4].
- (5) Liquid supply pressure oscillations [5].

Various mathematical expressions for mean drop size have been proposed [6, 7, 8, 9, 10]. Among these correlations, the most widely quoted is that of Nukiyama and Tanasawa [6] which has been used extensively in estimating drop sizes in high energy venturi scrubbers. The experimental studies of Boll, et. al. [10], Lewis, et. al. [11], and Hrubycky [12] showed that the applicability of the Nukiyama-Tanasawa equation is limited to high relative velocities and low liquid-to-gas ratios. It is not an appropriate model for ejector scrubbers which generally use mechanical atomization nozzles. For this reason, the drop size distribution was measured experimentally in the present study.

Correspondence concerning this paper should be sent to Gordon Lewandowski.

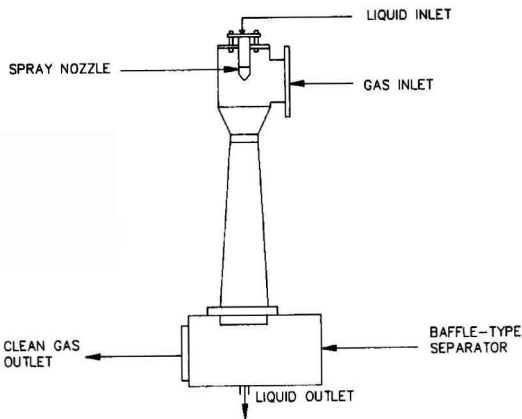


Figure 1. Schematic of ejector venturi scrubber.

### Methods of Drop Size Analysis

Several methods have been reported in the literature for determining drop size distributions. Of these methods, freezing the droplets and sieving them into size fractions [13], or collecting droplets on slides [14] are impractical for the high liquid flow rates encountered in scrubber operation. Also, the measurement of light transmittance [10] is only an indirect method of droplet size analysis. As a result, the method chosen in the present study was to take stop-action photographs of the spray.

### Fluid Flow in Ejector Venturi Scrubbers

Most of the experimental and theoretical fluid flow studies that are found in the literature are on high energy venturi scrubbers. The studies on ejector pumps mainly concentrate on one-component one-phase systems, two-component one-phase systems, or one-component two-phase systems. There are very few fluid flow studies on ejector venturi scrubbers, which are two-component, two-phase systems.

Previous ejector studies include an analysis of the two-phase mixing process in a cylindrical throat [15, 16], and a one-dimensional relationship for the ejector pump including frictional losses [17, 18].

Harris [19] determined that in a given ejector venturi scrubber the flow capacity can be increased by using a longer nozzle with higher liquid flow rates. He also calculated the energy requirements of the 12 inch Schutte and Koerting ejector venturi scrubber for various liquid and gas flows.

Witte's [20] analysis included a study of compressibility effects. He proposed to use a dimensionless number to evaluate the performance of the ejector pump.

Bhat, Mitra, and Roy [21] also made a theoretical analysis of the system on the basis of macroscopic momentum and mechanical energy balance equations. However, in their analysis they assumed the pressures at the nozzle exit and the throat entrance were equal, and they neglected the expansion of the liquid jet in that region. Also, loss of liquid to the walls of the venturi was not considered.

After considering these models, and noting the highly turbulent conditions in the scrubber, it was decided in the present study to utilize the mechanical energy balance, taking into consideration the loss of liquid spray to

the walls, and incorporating the experimentally determined pressure distribution.

### Gas Absorption in Ejector Venturi Scrubbers

Only a few theoretical and/or experimental studies of gas absorption in venturi scrubbers were found in the literature, and most of these studies were for high energy venturi scrubbers [22-29]. The total mass transfer in the ejector venturi scrubber is a function of mass transfer to single drops, integrated over the size distribution. Some work has been done on laminar jets [30-32]. However, no prior work was found on mass transfer to droplets in atomized jets.

### PROPOSED FLUID FLOW MODEL FOR THE EJECTOR VENTURI SCRUBBER

In this work, the fluid flow through an ejector venturi scrubber is described by a series of mechanical energy balances.

### Description of the Atomization Process

The helical vanes of the nozzle (Figure 2) impart a tangential velocity to the liquid jet, which aids the atomization process. The gas and atomized droplets mix in the throat section, where momentum is transferred from the liquid to the gas. In the diffuser, the static pressure of the gas continues to increase at the expense of the kinetic energy of the mixture (largely that of the liquid droplets, since the mass of the gas is relatively small).

### Fluid Flow Equations

Application of mechanical energy and material balances for an isothermal system produce the following expressions (which take into account loss of liquid to the scrubber walls):

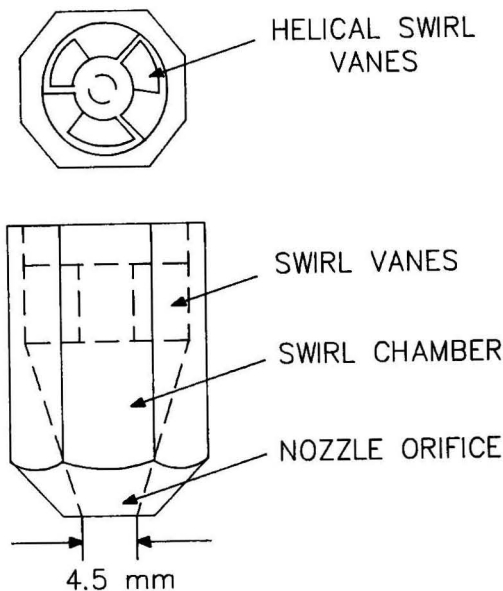


Figure 2. Atomizing nozzle.

(1) Mechanical Energy Balance for Liquid from Nozzle to Throat:

$$\frac{P_o - P_t}{\rho_L} + \frac{V_{Li}^2}{2g_c} \left[ \left( \frac{A_n}{A_{Lo}} \right)^2 - 1 + K_n \right] + \frac{g}{g_c} (L_o - L_t) = 0$$

(2) Mechanical Energy Balance for Gas from Entry to throat:

$$\frac{RT}{M_g} \ln \frac{P_o}{P_s} + \frac{V_{gs}^2}{2g_c} \left[ \left( \frac{A_{gs}P_s}{A_{go}P_o} \right)^2 - 1 + K_e \right] + \frac{g}{g_c} (L_o - L_s) = 0$$

(3) Mechanical Energy Balance for the Throat Section:

$$\begin{aligned} \frac{RT}{M_g} \ln \frac{P_t}{P_o} + \frac{Q_{Li}}{2Q_{gs}} \frac{M_g P_s}{RT} \left[ \left( \frac{L_o - L_t}{L_t - L_t} \right)^2 + 1 \right] (P_t - P_o) \\ + \left( \frac{A_{gs}P_s}{A_{go}P_o} \right)^2 \cdot \frac{V_{gs}^2}{2g_c} \left[ \frac{P_o^2}{P_t^2} - 1 + K_t \right] \\ + \frac{\rho_L Q_{Li}}{P_s M_g} \frac{1}{RT} \frac{Q_{gs}}{Q_{gs}} \left( \frac{A_n}{A_{Lo}} \right)^2 \frac{V_{Li}^2}{2g_c} \left[ \left( \frac{L_o - L_t}{L_t - L_t} \right)^2 - 1 + K_t \right] \\ + \frac{g}{g_c} (L_t - L_o) + \frac{g \rho_L Q_{Li}}{g_c \frac{P_s M_g}{RT} Q_{gs}} \left[ \left( \frac{L_o - L_t}{L_t - L_t} \right)^2 L_t - L_o \right] = 0 \end{aligned}$$

(4) Mechanical Energy Balance for the Diffuser Section:

$$\begin{aligned} \frac{RT}{M_g} \ln \frac{P_d}{P_t} \\ + \frac{Q_{Li}}{2Q_{gs}} \frac{M_g P_s}{RT} \left( \frac{L_o - L_t}{L_t - L_t} \right)^2 \left[ \left( \frac{L_t - L_t}{L_d - L_t} \right)^2 + 1 \right] (P_d - P_t) \\ + \left( \frac{A_{gs}P_s}{A_{gt}P_t} \right)^2 \frac{V_{gs}^2}{2g_c} \left[ \frac{P_t^2}{P_d^2} - 1 + K_d \right] \\ + \frac{\rho_L Q_{Li}}{P_s M_g} \frac{1}{RT} \frac{Q_{gs}}{Q_{gs}} \left( \frac{A_n}{A_{Lo}} \right)^2 \frac{V_{Li}^2}{2g_c} \left( \frac{L_o - L_t}{L_t - L_t} \right)^6 \\ \cdot \left[ \left( \frac{L_t - L_t}{L_d - L_t} \right)^2 - 1 + K_d \right] + \frac{g}{g_c} (L_d - L_t) \\ + \frac{g}{g_c} \frac{\rho_L Q_{Li}}{P_s M_g} \frac{1}{RT} \frac{Q_{gs}}{Q_{gs}} \left( \frac{L_o - L_t}{L_t - L_t} \right)^2 \cdot \left[ \left( \frac{L_t - L_t}{L_d - L_t} \right)^2 L_d - L_t \right] = 0 \end{aligned}$$

The following assumptions were made during the development of the fluid flow model:

- (1) The ideal gas is isothermally compressed from the scrubber inlet to diffuser outlet.
- (2) Heat rejection to the liquid from the compressed gas and from dissipation of frictional energy cause a negligible rise in liquid temperature.
- (3) Prior to mixing in the throat, the liquid jet and the gas are separate phases.
- (4) Changes in gas solubility and average molecular weight between scrubber inlet and outlet are neglected.
- (5) Evaporation of the liquid is neglected in performing the material balances.

The scrubber dimensions, temperature, pressure distri-

bution, and the volumetric flow rates of the liquid and gas were provided to the model, and the frictional loss coefficients ( $K_n$ ,  $K_e$ ,  $K_t$  and  $K_d$ ) were calculated.

## PROCEDURES

### Photographic Experiments

A clear plastic scrubber, with dimensions similar to those of the commercial unit employed for the fluid flow experiments, was constructed for the photographic studies. The nozzle was a 3/8 inch 622-L Schutte and Koerting design with a 4.5 mm opening (Figure 2), producing a 15° spray angle.

After much trial-and-error experimentation, a photographic method was developed using Polaroid 667 ASA 3000 film and a 500 C/M Hasselblad camera, with 135 mm CF lens and bellows system. Illumination was provided by a short arc xenon flash lamp (FX-199), with FYD-505 Lite Pac and PS-302 power supply trigger module, from EG&G Electro Optics. The experiments were carried out in a completely dark room, and the exposure time was controlled by the flash duration, which was about 1 microsecond. The camera was set at 10 inches (25 cm) from the mid-plane of the ejector venturi scrubber, and the flash lamp was installed 1.5 feet (46 cm) to the side. The power output of the flash lamp was increased by using an external 2  $\mu$ f capacitor.

The liquid flow rate was varied from 3 to 8 gpm (0.0114 to 0.0303 m<sup>3</sup>/min), in the atomizing range of the scrubber. However, at 8 gpm, there was too much turbulence to analyze the photographs. Most of the photographs were taken at 6 gpm liquid flow rate (.0227 m<sup>3</sup>/min), with 48 cfm air flow (1.36 m<sup>3</sup>/min). The f stops of the camera were varied from f/5.6 to f/45, with best results obtained in most cases at f/22 or f/27.

### Fluid Flow Experiments

The experimental setup is shown in Figure 3. An Ametek 7010 ejector venturi (mounted on type 7040 baffle separator) was used for the fluid flow experiments. This scrubber is fabricated of carbon steel. Scrubbing liquid from the separator is drained to a storage tank, and recirculated back to the spray nozzle.

The liquid flow rate was measured by a rotameter installed on the water recycle line. The air flow rate was measured with a Hastings meter, calibrated against a pitot tube.

Three thermometers were installed: one at the air inlet pipe, and two others near locations *i* and *d* of the ejector scrubber. These temperatures were essentially constant at about 23°C.

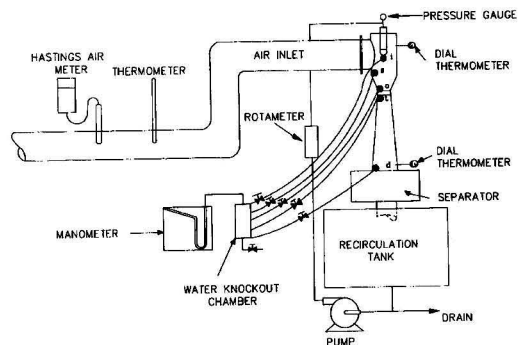


Figure 3. Experimental setup for fluid flow experiments.

Five pressure taps were installed at locations *i*, *s*, *o*, *t*, and *d*. Since very small pressure drops were expected, a slant type manometer was used. The manometer readings were in inches of water and the manometer fluid was 0.826 sp. gr. red oil.

### Gas Absorption Experiments

Anhydrous SO<sub>2</sub> was metered into the air inlet pipe at a concentration of 12,500 vppm. Gas samples were extracted simultaneously from the air inlet and separator exit, or from the diffuser exit and separator exit. The sampling train and method of analysis were derived from the U.S. EPA Method 6 for SO<sub>2</sub> analysis [33]. The scrubbing liquid was a recirculated .0001M NaOH solution.

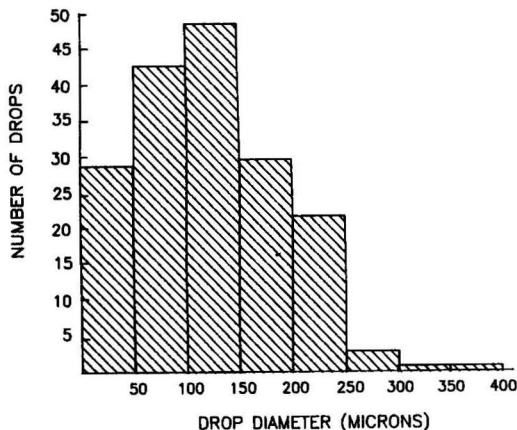


Figure 4. Droplet size distribution.

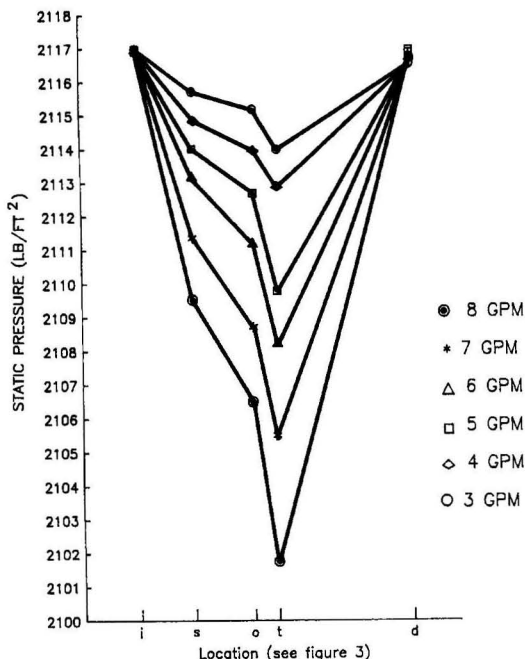


Figure 5. Ejector venturi scrubber static pressure distribution.

TABLE 1. EMPIRICAL FRICTIONAL LOSS CONSTANTS OF THE FLUID FLOW MODEL

$Q_L$	(ft <sup>3</sup> /min)	$Q_D$	$K_n$	$K_r$	$K_s$	$K_d$
1.069		64	0.777	1.94	0.854	0.361
.936		56	0.778	4.28	0.895	0.299
.802		48	0.780	4.41	0.672	0.175
.668		40	0.782	3.90	0.753	0.209
.535		32	0.786	5.17	0.680	0.440
.401		24	0.794	5.75	0.779	0.415
Avg. —		—	0.783	4.24	0.772	0.317

## RESULTS AND DISCUSSION

### Drop Size Distribution

The drop size distribution was determined from photographs taken just above the entrance to the venturi throat. The projected area of the liquid droplets was measured on enlargements of the photographs. A diameter of 1 mm on the enlargement would actually be 0.474 mm in the spray.

Once the actual diameters and the number of drops in each size had been determined, the volume mean diameter was calculated using the following formula:

$$D_r = \left[ \frac{\sum n_i D_i^3}{\sum n_i} \right]^{1/3}$$

The volume mean diameter was determined to be 155 microns, and the sizes of the droplets ranged from 34 microns to 563 microns (with the size distribution shown in Figure 4).

### Area Occupied by the Liquid

The area occupied by the liquid drops at the entrance of the throat section ( $A_{Lo}$ ) is required for the fluid flow model. This was calculated by considering a cylindrical volume element at the throat entrance, with diameter equal to the throat diameter ( $D_t$ ) and height equal to the volume mean diameter ( $D_r$ ). Within this element, the volume ratio of liquid-to-gas at any instant is equal to the ratio of the volumetric flow rates:

$$\frac{V_{Lo}}{V_{go}} = \frac{A_{Lo} D_r}{(A_t - A_{Lo}) D_r} = \frac{Q_{Lo}}{Q_{go}}$$

By this equation,  $A_{Lo}$  was calculated to be 0.0516 square inches (.330 cm<sup>2</sup>). At a volume mean diameter of 155 μm, the liquid area is equivalent to 560 drops per square inch on a horizontal plane just above the throat entrance.

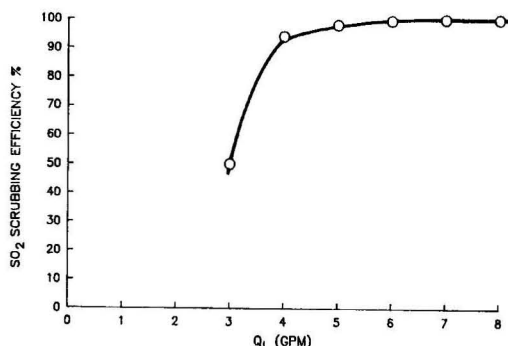


Figure 6. Overall SO<sub>2</sub> scrubbing efficiency (with .0001M NaOH).

## Pressure Distribution (see Figure 5)

There was a sharp pressure drop between the nozzle tip and the throat exit (locations *i* and *t*), followed by a pressure recovery in the diffuser section. The pressure recovery was achieved at the expense of the kinetic energy of the gas/liquid mixture.

The pressure distribution profile flattened as the liquid flow rate decreased. At 8 gpm liquid flow rate the pressure drop between nozzle tip and throat exit was 15.3 psf (.733 kPa), while at 3 gpm liquid flow rate the pressure drop between the same two locations was only 3.0 psf (.144 kPa). This is due to the decreased kinetic energy of the liquid jet.

## Frictional Loss Constants

The empirical frictional loss constants of the fluid flow model were calculated using the results of the photographic analysis and pressure distribution profile [34]. These constants are listed in Table I. For the most part, the individual *K* values are fairly consistent, and their order of magnitude is typical of those for other fluid flow phenomena [35, 36].

## Sulfur Dioxide Scrubbing Efficiency

Figure 6 shows the variation with liquid flow rate of the scrubbing efficiency of the ejector venturi scrubber/

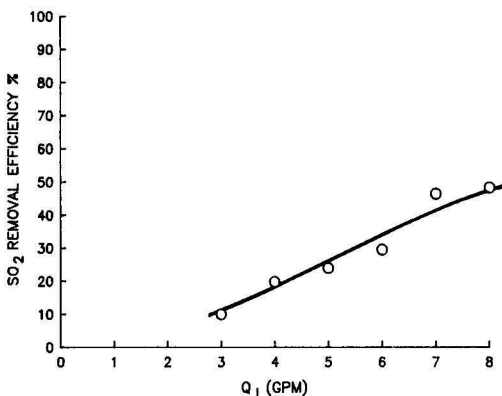


Figure 7. SO<sub>2</sub> removal efficiency in the separator only.

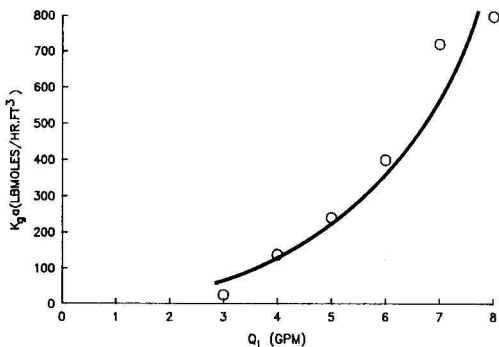


Figure 8. Variation of volumetric mass transfer coefficient (*K<sub>g</sub> a*) with liquid flow rate.

separator system. There is a sharp increase in efficiency as the liquid flow rate reaches the complete atomization regime. Above 4 gpm liquid flow, the efficiency rises from 94 to 99.97%.

The fractional scrubbing efficiency achieved in the baffle separator was determined separately (see Figure 7). As the liquid flow rate decreased from 8 gpm to 3 gpm, the separator efficiency also dropped from 48% to 10%.

The volumetric mass transfer coefficient (*K<sub>g</sub> a*) for the SO<sub>2</sub>-NaOH system was calculated from experimental results, and at 8 gpm liquid flow it was determined to be 800 pound moles per hour per cubic foot of scrubber volume (12,800 kg-mole/hr-m<sup>3</sup>). As the liquid flow rate decreased to 3 gpm, the mass transfer coefficient also decreased (Figure 8) down to 25 pound moles per hour per cubic foot of scrubber volume (400 kg-mole/hr-m<sup>3</sup>). This is primarily due to the decreased interfacial area at lower liquid flow rates.

The interfacial area, in square feet per cubic foot of scrubber volume, is represented by the following relationship:

$$a = \frac{1}{(1 + Q_{gs}/Q_{li})} \left( \frac{6}{D_r} \right)$$

At full atomization, '*a*' was approximately 200 square feet per cubic foot of scrubber volume (650 m<sup>2</sup>/m<sup>3</sup>). Therefore, the overall mass transfer coefficient was calculated to be 4.0 lb-mole/hr-ft<sup>2</sup> of interfacial area (20 kg-mole/hr-m<sup>2</sup>).

## NOTATION

- a* = interfacial area of spray droplets (ft<sup>2</sup>/ft<sup>3</sup> of scrubber volume) (or m<sup>2</sup>/m<sup>3</sup> of scrubber volume)
- A<sub>n</sub>* = cross-section of nozzle tip (.0247 in.<sup>2</sup>, or .159 cm<sup>2</sup>)
- A<sub>l,o</sub>* = horizontal area occupied by liquid droplets at top of throat (.0516 in.<sup>2</sup>, or .33 cm<sup>2</sup>)
- A<sub>gs</sub>* = cross-section of gas entrance (12.6 in.<sup>2</sup>, or 81 cm<sup>2</sup>)
- A<sub>g,o</sub>* = *A<sub>t</sub>* - *A<sub>l,o</sub>*
- A<sub>t</sub>* = cross-section of throat (3.14 in.<sup>2</sup>, or 20.3 cm<sup>2</sup>)
- D<sub>i</sub>* = diameter of a droplet in the spray
- D<sub>r</sub>* = volume mean diameter of droplets (155 μm)
- D<sub>t</sub>* = diameter of throat (2 inches, or 5 cm)
- g* = acceleration of gravity
- g<sub>c</sub>* = units conversion factor
- K<sub>g</sub>* = mass transfer coefficient (lb-moles/hr-ft<sup>2</sup> of interfacial area) or kg-moles/hr-m<sup>2</sup> of interfacial area).
- K<sub>d</sub>*, *K<sub>e</sub>*, *K<sub>n</sub>*, *K<sub>t</sub>* = empirical frictional loss constants in mechanical energy balances
- L<sub>o</sub>* - *L<sub>t</sub>* = height of throat (1 inch, or 2.5 cm)
- L<sub>i</sub>* - *L<sub>o</sub>* = distance from nozzle tip to throat (6-1/4 inches, or 15.9 cm).
- L<sub>s</sub>* - *L<sub>o</sub>* = distance from point 's' (Fig. 3) to throat (3 inches, or 7.6 cm).
- L<sub>t</sub>* - *L<sub>d</sub>* = height of diffuser section (14-1/4 inches, or 36 cm).
- M<sub>g</sub>* = average molecular weight of gas
- n<sub>i</sub>* = number of droplets of diameters *D<sub>i</sub>*
- P<sub>i</sub>*, *P<sub>s</sub>*, *P<sub>o</sub>*, *P<sub>t</sub>*, *P<sub>d</sub>* = static pressure of gas at points *i*, *s*, *o*, *t*, *d*—respectively (Fig. 3).
- Q<sub>l,o</sub>*, *Q<sub>g,o</sub>* = liquid and gas volumetric flows (respectively) at throat entrance
- Q<sub>l,i</sub>* = liquid volumetric flow rate from the nozzle
- Q<sub>gs</sub>* = gas volumetric flow entering the scrubber
- R* = universal gas constant
- T* = absolute temperature of gas
- V<sub>l,i</sub>*, *V<sub>l,o</sub>* = liquid velocities at nozzle exit and throat entrance (respectively)



$V_{gs}$ ,  $V_{go}$  = gas velocities at gas entrance and throat entrance (respectively)  
 $\rho_L$  = liquid density

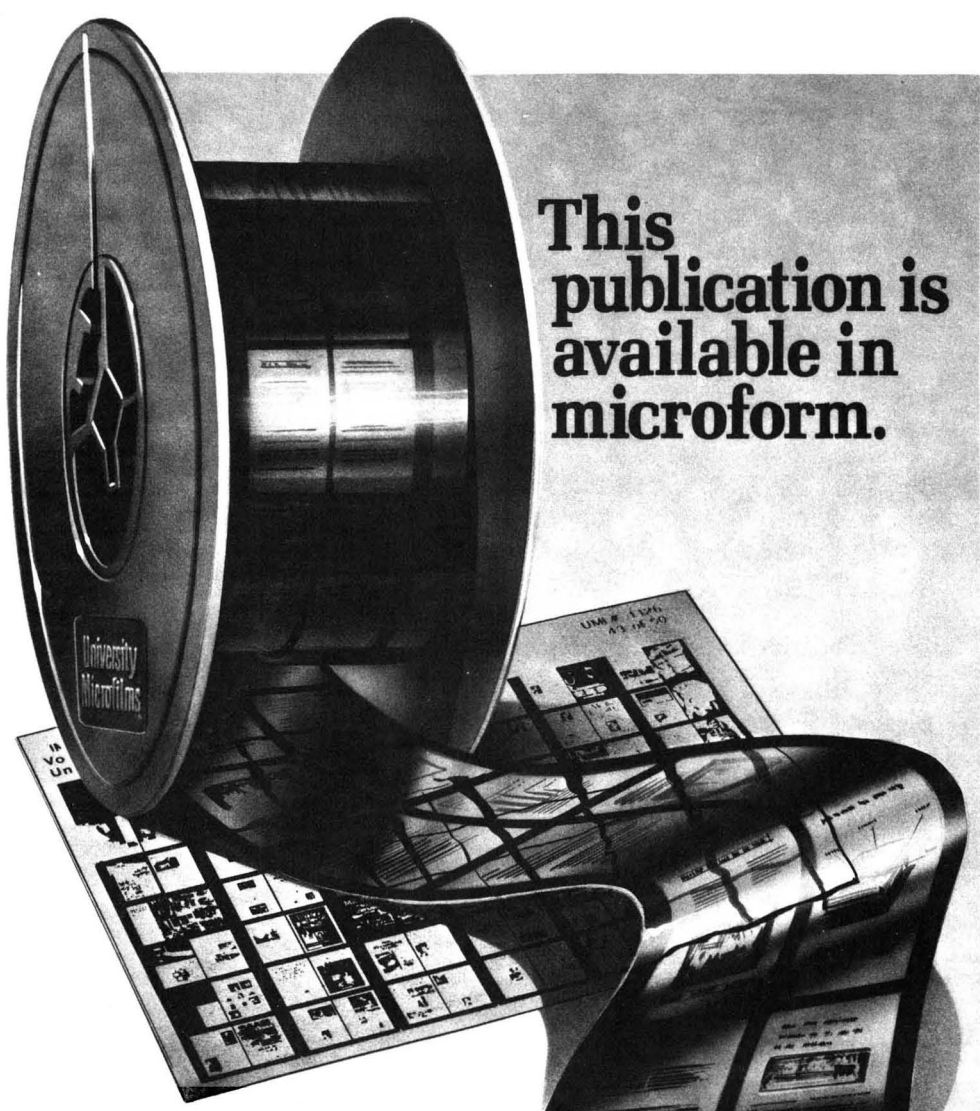
#### LITERATURE CITED

1. Castleman, R. A., "Mechanism of Atomization of Liquids," U.S. Natl. Bureau of Std. J. Res., 6, 281 (1931).
2. DeJuhasz, K. J., "Dispersion of Sprays in Solid Injection Oil Engines," Trans. Am. Soc. Mech. Eng. (OGP), 53, 65 (1931).
3. Bergwerk, W., "Flow Pattern in Diesel Nozzle Spray Holes," Proc. Inst. Mech. Eng., 173, 655 (1959).
4. Rupe, J. H., "On the Dynamic Characteristics of Free Liquid Jets and a Partial Correlation with Orifice Geometry," J. P. L. Technical Report, No. 31, p. 207 (1962).
5. Giffen, E. and A. Muraszew, *The Atomization of Liquid Fuels*, John Wiley and Sons, NY (1953).
6. Nukiyama, S. and Y. Tanasawa, "Experiments on the Atomization of Liquids in an Air Stream," Trans. Soc. Mech. Eng. (Japan), Vols 4-6, Reports 1-6, 1938-40.
7. Mugele, R. A., "Maximum Stable Droplets in Dispersoid," *AIChE J.*, 6, 3-10 (1960).
8. Gretzinger, J. and W. R. Marshall, "Characteristics of Pneumatic Atomization," *AIChE J.*, 7, 312-318 (1961).
9. Kim, K. Y. and W. R. Marshall, "Drop Size Distribution from Pneumatic Atomizers," *AIChE J.*, 17, 575-584 (1971).
10. Boll, R. H., L. R. Flais, P. W. Maurer, and W. L. Thompson, "Mean Drop Size in a Full Scale Venturi Scrubber Via Transmissometer," *JAPCA*, 24, 934-938 (1974).
11. Lewis, H. C., D. G. Edward, M. J. Goglia, R. I. Rice, and L. W. Smith, "Automization of Liquids in High Velocity Gas Streams," *Ind. Eng. Chem.*, 40, 67-74 (1948).
12. Hrubecky, H. F., "Experiments in Liquid Atomization by Air Streams," *J. Applied Physics*, 29, 572-578 (1958).
13. Longwell, J. P., "Fuel Oil Atomization," Ph.D. Thesis, Massachusetts Institute of Technology (1943).
14. Fraser, R. P. and P. Eisenklam, "Liquid Atomization and the Drop Size of Sprays," Trans. Inst. Chem. Eng. (USA), 34, 294-319 (1956).
15. Folsom, R. G., "Jet Pumps with Liquid Drive," *Chem. Eng. Prog.*, 44, 765-770 (1948).
16. Takashima, Y., "Studies on Liquid Jet Gas Pumps," *J. Sci. Res. Inst. (Tokyo)*, 46, 230-246 (1952).
17. Higgins, H. W., "Water Jet Air Pump Theory and Performance," M.S. Thesis, The Pennsylvania State University (1964).
18. Betzler, R. L., "The Liquid-Gas Jet Pump Analysis and Experimental Results," M.S. Thesis, The Pennsylvania State University (1969).
19. Harris, L. S., "Energy and Efficiency Characteristics of the Ejector Venturi Scrubber," *JAPCA*, 5, 302 (1965).
20. Witte, J. H., "Mixing Shocks in Two Phase Flow," *J. Fluid Mechanics*, 36, (Part 4), 639-655 (1969).
21. Bhat, P. A., A. K. Mitra, A. N. Roy, "Momentum Transfer in a Horizontal Liquid Jet Ejector," *Canadian J. Chem. Eng.*, 50, 313-317 (1972).
22. Boyadzhiev, K., "On the Optimal Flow of Liquid During Chemisorption in a Venturi Tube," *Int. Chem. Eng. (Bulgaria)*, 4, 22-26 (1964).
23. Downs, W. and G. A. Atwood, "Mathematical Model for Gas Absorption in a Venturi Scrubber," paper presented at AIChE National Meeting, Detroit (1973).
24. Kuznetsov, M. D. and V. I. Ortawski, "Rate of Chemisorption in A Venturi Type Apparatus," Ph.D. Thesis, University of Florida (1970).
25. Raman, S., "Gas Absorption in a Low Energy Venturi Scrubber," Ph.D. Thesis, University of Akron (1983).
26. Wen, C. Y. and S. Uchida, "Absorption of Sulfur Dioxide by Alkaline Solutions in Venturi Scrubber Systems," *Ind. Eng. Chem. (Process Des. Develop.)*, 12, 437 (1973).
27. Johnstone, H. F., M. C. Tassler, and R. B. Feild, "Gas Absorption and Aerosol Collection in a Venturi Atomizer," *Ind. Eng. Chem.*, 46, 1601-1608 (1954).
28. Virkar, P. D. and M. M. Sharma, "Mass Transfer in Venturi Scrubbers," *Canadian J. Chem. Eng.*, 53, 512-516 (1975).
29. Volgin, B. P., T. F. Efimova, and M. S. Gofman, "Absorption of Sulfur Dioxide by Ammonium Sulfite-Bisulfite Solution in a Spray Type Venturi Scrubber," *Khimicheskaya Promyshlennart*, 43, 132-136 (1967).
30. Burkholder, H. C. and J. C. Berg, "The Effect of Mass Transfer on Liquid Jet Breakup," *AIChE J.*, 20, 863 (1974).
31. Duda, J. L. and J. S. Vrentas, "Fluid Mechanics of Laminar Liquid Jets," *Chem. Eng. Sci.*, 22, 855 (1967).
32. Huang, Y.-F., "Mass Transfer During Drop Formation Under Jetting Conditions," Ph.D. Thesis, University of Kentucky (1976).
33. U.S. EPA, Code of Federal Regulations, Title 40, Protection of Environment, Chapter 1, Part 60, Appendix A, Method 6: "Determination of Sulfur Dioxide Emissions from Stationary Sources" (1983).
34. Atay, I., "Fluid Flow and Gas Absorption in an Ejector Venturi Scrubber," Ph.D. Thesis, New Jersey Institute of Technology (1986).
35. McCabe, W. L. and J. C. Smith, *Unit Operations in Chemical Engineering*, 4th ed., McGraw-Hill, NY (1985).
36. Bird, Stewart, Lightfoot, *Transport Phenomena*, John Wiley, NY (1960).

**Iclal Atay** was a graduate student at the New Jersey Institute of Technology at the time of this research, and is now with the New Jersey Department of Environmental Protection in Trenton, New Jersey.

**Gordon Lewandowski** is a Professor of Chemical Engineering at NJIT and holds B.S. and M.S. degrees from the Polytechnic Institute of Brooklyn as well as a D. Eng. Sc. from Columbia University, all in chemical engineering. After several years in industry, he joined the faculty at NJIT, where his research has been in various aspects of pollution control.

**Richard Trattner** is a Professor of Environmental Science and Chemistry at NJIT. He received degrees in chemistry from CCNY (B.S.), Brooklyn College (M.A.), and CUNY (Ph.D.), with four years of industrial experience in between. After receiving his doctorate, he joined the faculty at NJIT, where his research has been primarily in the fields of environmental monitoring and control.



**This  
publication is  
available in  
microform.**

University Microfilms International reproduces this publication in microform: microfiche and 16mm or 35mm film. For information about this publication or any of the more than 13,000 titles we offer, complete and mail the coupon to: University Microfilms International, 300 N. Zeeb Road, Ann Arbor, MI 48106. Call us toll-free for an immediate response: 800-521-3044. Or call collect in Michigan, Alaska and Hawaii: 313-761-4700.

**University  
Microfilms  
International**

Please send information about these titles:

Name \_\_\_\_\_

Company/Institution \_\_\_\_\_

Address \_\_\_\_\_

City \_\_\_\_\_ State \_\_\_\_\_ Zip \_\_\_\_\_

Phone ( ) \_\_\_\_\_

# find information fast

document  
delivery

fast  
precise  
searches

**ESL**  
information  
services

save time  
and money

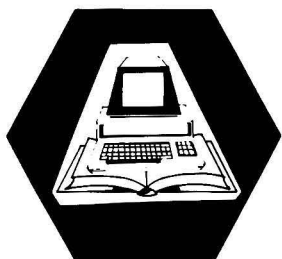
online  
information  
retrieval

comprehensive  
bibliographies

ESL Information Services addresses the special needs of the Engineering and Technological community. Through the DIALOG information retrieval system, we can survey 'online' 15 years of the worldwide engineering and scientific literature in a few minutes at costs that are a fraction of manual searches.

## WHAT ESL INFORMATION SERVICES HAS TO OFFER YOU

- Fast precise searches of the Engineering Literature
- Immediate access to engineering journals, numerous conference proceedings, reports, and books
- Over 65 databases covering engineering, physics, computers, energy, materials, patents, and chemistry
- Flexible and extensive search terms - authors, title words, subject categories, chemical abstracts register numbers
- More for your money and time... save hours of library research over manual techniques
- Document delivery... tap the vast resources of the Engineering Societies Library's engineering and technological literature... over 5000 serials from some 50 countries in 25 languages



For more information on this indispensable research tool, please call or write:

**ESL Information Services**

## **Engineering Societies Library**

345 East 47th Street New York, New York 10017 (212) 705-7610

**We've been number one since the beginning because we initiate...**



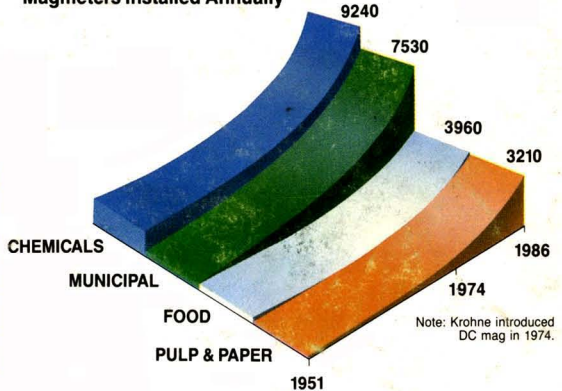
# ...PROGRESS

Can you say even one of these about your present flow meter?

- High accuracy
- High rangeability
- High chemical & erosion resistance
- No pressure loss
- No moving parts
- No obstructions
- No maintenance



Magmeters Installed Annually



In 1951 Krohne was the only magmeter manufacturer.

Typical 1/2" Magmeter System

	1951	1961	1971	1986
Accuracy (Wet Calibrated)	1.5% full scale	1% full scale	0.5% reading + 0.5% full scale	0.2% of rate
Min. Conductivity Required ( $\mu\text{mho/cm}$ )	100	100	20	0.5
Volt Amps	214.5	242	26.4	20
Price (Constant Dollars)	\$8492	\$6636	\$4074	\$3368

**KROHNE**



Krohne America, Inc.  
One Intercontinental Way  
Peabody, MA 01960  
(617) 535-6060  
Telex: 4430214

Krohne America, Inc.  
983 Old Eagle School Road  
Suite 602  
Wayne, PA 19087  
(215) 688-8400

Krohne America, Inc.  
99 Detering Street  
Suite 250  
Houston, TX 77007  
(713) 880-4371

Krohne America, Inc.  
P.O. Box 934  
Palatine, IL 60067  
(312) 934-8169

Send for Magmeter Facts

