

NOVEMBER 1985

# ENVIRONMENTAL PROGRESS



# Three Mile Island Cleanup

## Experiences, Waste Disposal, And Environmental Impact

Lester J. King and James H. Opelka,  
Editors

*"The papers included in this book deal with the experiences and problems in cleaning up Three Mile Island Unit-2 (TMI-2) following the accident . . . and the waste disposal and environmental impacts of the cleanup.*

*The material damages and losses resulting from the accident are very high. Cleanup will take many years and . . . costs will certainly be somewhere near \$1 billion" (from the foreword).*

### Contents:

- Three Mile Island Unit 2 (TMI-2) Reactor Building Venting Experience.
- TMI Containment Entry Program.
- Water Decontamination Process Improvement Tests and Considerations.
- TMI-2 Technical Information and Examination Program.
- Generation, Classification, Treatment and Disposal of Solid Waste Forms Resulting from Cleanup of TMI-2.
- Three Mile Island Waste Management: A DOE Perspective.
- Radiation Effects on Ion Exchange Materials Used in Waste Management.
- Three Mile Island Zeolite Vitrification Demonstration Program.

Material presented was selected from papers presented at AIChE's National Meeting in Detroit, Michigan, August 16-19, 1981.

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

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Volume 4

Contents

Number 4

## Editorial

*J. A. Scher* ..... N3

**Environmental Shorts** ..... N5

## 1984 Survey of Research on Environmental Pollution—Its Sources, Fate, Effects, and Control

*I. Atley Jefcoat* ..... 217

## Combined SO<sub>2</sub>/NO<sub>x</sub> Removal from Flue Gas

*James T. Yeh, Richard J. Demski, Joseph P. Strakey and James I. Joubert* ..... 223

## Oxidation of 2-Chlorophenol Using Ozone and Ultraviolet Radiation

*Shahab R. Khan, Ching R. Huang and Joseph W. Bozzelli* ..... 229

## The Removal of Trace Levels of Dioxins from Water by Sorption on Modified Clay

*Keeran R. Srinivasan, H. Scott Fogler, Erdogan Gulari, Tim Nolan and Jerome S. Schultz* ..... 239

## Design and Operating Problems of Hazardous Waste Incinerators

*Joseph J. Santoleri* ..... 246

## Effect of Ozonation and UV Irradiation on Biorefractory Organic Solutes in Oil Shale Retort Water

*B. M. Jones, G. W. Langlois, R. H. Sakaji and C. G. Daughton* ..... 252

## A Mathematical Model of Settling Velocity Enhancement by Kinetic Control

*Karl B. Schnelle, Jr., K. D. Schnelle, Steve J. Gibbs and David J. Wilson* ..... 259

## Separation of Metals in Wastewater Sludge by Centrifugal Classification

*Carol Ann Fronk, Joseph B. Farrell and William Strachan* ..... 269

**Washington Environmental Newsletter** ..... N7

**Environmental Index** ..... N9

**Cover: Cleanup operation of a Gulf Coast oil spill on a Texas beach. @1985 Lou Witt, Shostal Associates.**

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### Section 112: Hazardous Air Pollutants Clean Air Act

by J. A. Scher

The Clean Air Act of 1970 (amended in 1977) enacted by the Congress of the United States requires the Environmental Protection Agency to develop a listing of hazardous air pollutants. Section 112 of the Act, entitled "National Emission Standards for Hazardous Air Pollutants," establishes the primary regulatory framework for regulating hazardous air pollutant emissions. Since the advent of the Clean Air Act and Section 112, the EPA has listed seven hazardous air pollutants and has promulgated regulations for only the first five. The seven are as follows:

- Mercury
- Benzene
- Beryllium
- Radionuclides
- Asbestos
- Inorganic Arsenic
- Vinyl Chloride

The Air Quality Task Force of AIChE has identified the following six impediments to effectively regulating hazardous air pollutants:

1. The definition of "Hazardous Pollutant" results in an inherent difficulty in relating statistical data on mortality to pollutant concentrations for short and long term effects.
2. Regulating some air pollutants to a point of "ample margin of safety" may be synonymous with zero emissions because of lack of information on threshold levels.
3. Health effects and statistical data for air pollutants are often inadequate to generate or support standards.
4. There is almost total disregard of any cost/benefit analysis in establishing individual and "class" emission standards. Although the cost/benefit concept is being used by the EPA in other regulatory areas, it is not allowed by the Clean Air Act.
5. The use of a national standard is often

too rigid because of regional and local implications relative to both technical and economic issues.

6. There is a general lack of background ambient air quality data on individual pollutants to support either the need for or the level of proposed standards.

The Air Quality Task Force of AIChE proposes that certain modifications to the existing Section 112 of the Clean Air Act be made. These are:

1. Focus upon pollutants which have the greatest potential for health hazard reduction.
2. Create a rigorous scientific procedure including peer review to develop the necessary background data encompassing health effects of individual pollutants.
3. Remove the "ample margin of safety" clause and replace with words encompassing procedures committed to a reasonable risk assessment and risk management.
4. Consider the effects of standards setting upon our industrial network and economic climate as well as upon public health and welfare.

The Air Quality Task Force of AIChE recognizes that there are many complicating factors in writing legislation and proposing regulations to achieve air quality goals compatible with both protection of public health and welfare and the maintenance of the productive capacity of our country. We believe that all of the deficiencies should be addressed by Congress in order to rectify the present regulatory problems.

---

*J. A. "Coby" Scher is a member of the Advisory board of Environmental Progress, and a past Chairman of the Environmental Division of AIChE. He is Vice President of Resource Engineering Inc., Houston, TX.*

## Environmental Shorts

### More Groundwater Protection Needed, Monsanto Executive Says

Government at the local, state, and federal levels can strengthen existing programs to curb pollution of groundwater, provided "we continue moving at a deliberate pace," Harold J. Corbett, senior vice president of Monsanto Co. said at the annual National Association of Towns and Townships meeting in September. "The country as a whole is keenly aware of the importance of groundwater to our well-being, and we are coming to grips with how to best safeguard and manage it."

Corbett stressed that "we are acting on groundwater with sufficient time to do the job thoughtfully and well," and do not face the sort of emergency situa-

tion that prevailed on air and water pollution in the late 1960's.

Citing EPA estimates of high levels of contamination on one percent of all groundwater and three percent of groundwater used for public drinking supplies, he said "some communities with particular grave groundwater pollution problems have had to seek alternative sources of drinking water." He described the federal laws and state programs now in place to protect groundwater and maintained that, "much of industry's consciousness... has been raised on the groundwater issue." He added that, "state and local governments should retain the primary respon-

sibility for developing groundwater management programs," using technical guidance and finding support from the federal government.

"Clearly, we cannot simply write off polluted groundwater that may be needed for drinking or other high purity uses. On the other hand, this nation cannot afford nor would it make any sense, to rigorously clean up every polluted groundwater source, regardless of its present or projected use. We have to set priorities, and for groundwater, this means considering uses and levels of contamination in deciding where to concentrate our protection and cleanup efforts." Corbett concluded.

### Scientists Seek Clues to Glacial History in Antarctica

Scientists this month will start the most intensive study yet of a mountainous region of Antarctica that holds clues to the glacial history of that continent as well as fossils of vertebrates that flourished more than 240 million years ago.

The major scientific effort will concentrate on the Beardmore Glacier area in the Transantarctic Mountains, midway between McMurdo Station, the principal U.S. scientific facility on the continent, and the South Pole. Beardmore, approximately 100 miles long and between 15 and 30 miles wide, is one of the glaciers draining the vast East Antarctic Ice Sheet into the Ross Ice Shelf. Because it lies near the center of the continent and contains extensive ice-

free terrain with well-preserved glacial deposits, the Beardmore Glacier area is an important testing ground for opposing hypotheses of antarctic ice sheet behavior during global ice ages.

This project is one of approximately 87 scientific efforts in several disciplines to be undertaken by more than 300 researchers in Antarctica this season, the 30th consecutive year of U.S. scientific activity there. The National Science Foundation funds and coordinates all U.S. activities on this continent.

The Beardmore project will be conducted between mid-November and late January, 1986, and participants will be from 12 American universities and col-

leges, the U.S. Geological Survey and New Zealand researchers. Dr. David H. Elliot, a professor of geology at Ohio State University and director of the University's Institute of Polar Studies, will lead the U.S. contingency.

According to Dr. Elliot, "the history of the growth and fluctuation of the Antarctic Ice Sheets may have started more than 30 million years ago. Our understanding of the timing and magnitude of the fluctuations is rudimentary. One of the objectives of studying glacial deposits is to try to establish more accurately the growth and decay of the East Antarctic Ice Sheet and the times at which it may have covered the Transantarctic Mountains.

### Dartmouth's Thayer School Set to Open Major Academic Cold Region Center

Dartmouth College's Thayer School of Engineering will establish the nation's first major center for cold regions science and engineering within an academic setting.

The Industry/University Center for Cold Regions Science and Engineering at the Thayer School is made possible by a five-year, \$250,000 grant from the National Science Foundation and nearly twice that amount in support from industry, particularly oil companies interested in Arctic exploration.

"Once established, the new center will constitute a unique organization which will advance Arctic engineering

and aid the economic development of the country," Dr. Erland M. Schulson, director of the new center said.

Recent U.S. Geological Survey estimates indicate that the total undiscovered domestic oil and gas reserves—nearly 60 percent of the oil and 50 percent of the gas,—may lie beneath ice-encrusted waters off the Alaskan coast. Blocking the way to much of those resources are major obstacles such as the icing of equipment and movement of thick sheets of ice against off-shore drilling rigs or ships.

Thayer School is particularly suited for this kind of training and research,

Shulson said, "because of its tremendous computing facilities, emphasis on interdisciplinary engineering, and our Ice Research Laboratory." This laboratory, established with earlier grants from the Department of Defense and Mobil Corp., is equipped with four cold rooms capable of operation at 50 degrees below zero and a specialized machine designed to test the strength and brittleness of ice under pressure. Moreover, the new center will build on the school's working relationship with the U.S. Army's Cold Regions Research and Engineering Laboratory (CRREL), located near the Dartmouth campus.

## Call for Papers Boston Summer 1986 AIChE Meeting Environmental Division Program

### **Emerging Techniques for Heavy Metals Separation**

Robert W. Peters, Chairman, School of Civil Engineering, Purdue University, West Lafayette, IN 47907; (317) 494-2191. Mriganka M. Ghosh, Vice Chairman, Department of Civil Engineering, Pennsylvania State University, University Park, PA 16802.

### **Liquid Phase Oxidation of Organics from Hazardous Wastewaters**

Danny Reible, Dept. of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803; (504) 388-1426.

### **Membrane Separation Processes for Pollution Control**

D. Bhattacharyya, Dept. of Chemical Engineering, University of Kentucky, Lexington, KY 40506; (606) 257-2794.

### **Chemical Engineering Fundamentals as Applied to the Environment**

L. J. Thibodeaux, Dept. of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803; (504) 388-1426.

### **Coal Tar Waste Sites: Treatment and Clean-up Needs**

John C. Craun, Chairman, Reilly Tar & Chemical Corp., 1500 South Tibbs Ave., Indianapolis, IN 46241; (317) 247-8141. Geoffrey J. Filby, Vice Chairman, Stone & Webster Engineering Corporation, P.O. Box 2325, Boston, MA 02107; (617) 589-7887.

### **Organo-Metallic and PCB Waste Contamination of New England Waterways**

Daniel K. Moon, Chemical Waste Management, Inc., Assembly Square Office Park, 5 Middlesex Ave., Somerville, MA 02145; (617) 623-5680.

### **Boston Harbor Clean-up**

Alfred E. Peloquin, US EPA—Region 1, JFK Bldg., P.O. Box 8714, Boston, MA 02114; (617) 223-3909.

### **Control of Atmosphere Discharges from Coal**

#### **Gasification—Combined Cycle Systems**

Neville Holt, Chairman, Electric Power Research Institute, 3412 Hillview Ave., P.O. Box 10412, Palo Alto, CA 94303; (415) 855-2503. Peter Knox, Vice Chairman, Ralph M. Parsons Co., 2712 Doresta San Marino, CA 91108; (818) 440-2889.

### **The New LUST Regulations—What They Mean to the Chemical and Oil Terminal Industries**

B. T. Delaney, Program Manager, CH2M Hill, 169 Ramapo Valley Rd., Oakland, NJ 07436; (201) 337-9200.

### **Air Toxics: Management Strategies and Technological Solutions for New Section 112 Pollutants**

William C. Zegel, President, Water and Air Research, Inc., P.O. Box 1121, Gainesville, FL 32602; (909) 372-1500.

### **Pesticides and Groundwater Contamination**

Anthony D. Cortese, Director, Tufts University Center for Environmental Management, Graves House, 18 Latin Way, Medford, MA 02115; (617) 628-5000 X 3486.

### **Risk Assessment and Management Applications at Uncontrolled Hazardous Waste Sites**

J. A. Scher, Vice President, Resource Engineering, 3000 Richmond Ave., Houston, TX 77098; (713) 520-9900.

### **Groundwater Protection—Waste Treatment Practices in the Electronics Industry: Practical Aspects of Treatment**

Paul Yaniga, Ground Water Technology, Routes 1 and 100, Chadds Ford, PA 19317; (215) 388-1466.

### **Groundwater Protection—Waste Treatment Practices in the Electronics Industry: Fundamentals of Treatment Technologies**

William Tambo, Chairman, Director of Technical Services, Wehran Engineering, 467 Lafayette Rd., Hampton, NH 03842; (603) 926-7887. Catherine N. Lowery, Vice Chairman, Senior Engineer, Wehran Engineering, 467 Lafayette Rd., Hampton, NH 03842; (603) 926-7887.

### **Institutional Barriers to Siting Central Regional/Hazardous Waste Treatment Facilities**

B. T. Delaney, Program Manager, CH2M-Hill, 169 Ramapo Valley Rd., Oakland, NJ 07436; (201) 337-9200.

### **Advanced Technology Alternatives to Landfilling Hazardous Waste**

Harry M. Freeman, Chairman, Research Program Manager, Hazardous Waste Engineering, US EPA Research Lab, Cincinnati, OH 45268; (513) 684-7696.

B. T. Delaney, Vice Chairman, Program Manager, CH2M-Hill, 169 Ramapo Valley Rd., Oakland, NJ 07436; (201) 337-9200.

### **Emerging Biological Treatment Processes for Leachate Treatment Including Genetic Engineering Issues**

Stanley A. Sojka, Chairman, Manager—Special Environmental Programs, Occidental Chemical Corp., Occidental Chemical Ctr., 360 Rainbow Blvd. South, Box 728, Niagara Falls, NY 14302; (716) 286-3084. Don Michelson, Vice Chairman, Dept. of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061; (703) 961-5157.

### **Environmental Audits in the Light of Bopal**

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### **Geotextiles, Membranes, and Other Barriers: Compatibility Issues**

Mary Ann Curran, US EPA, 26 West St. Clair, Cincinnati, OH 45268; (513) 684-7836.

### **Evaluation of New and Innovative Waste Treatment Facilities**

Edward D. Schroeder, Dept. of Civil Engineering, University of California—Davis, Davis, CA 95616; (916) 752-6757.

### **University Graduate Research in Environmental Control Fundamentals**

Robert L. Irvine, Chairman, Dept. of Civil Engineering, University of Notre Dame, Notre Dame, IN 46556; (219) 239-6306. Richard D. Siegel, Vice Chairman, Senior Environmental Consultant, Environmental Research & Technology, 696 Virginia Rd., Concord, MA 01742; (617) 369-8910. B. Tod Delaney, Vice Chairman, Program Manager, CH2M-Hill, 169 Ramapo Valley Rd., Oakland, NJ, 07436; (201) 337-9200.

### **Multimedia Environmental Issues**

James J. McKeown, Chairman, National Council for Air & Stream Improvement, Tufts University, Medford, MA 02155; (617) 381-3254. Robert L. Irvine, Vice Chairman, Dept. of Civil Engineering, University of Notre Dame, Notre Dame, IN 46556; (219) 239-6306.

### **Process Modification for Waste Minimization and Managing Environmental Risk**

Robert W. Rittmeyer, Chairman, Manager—Environmental Process Engineering, ERT, Inc., Porter Bldg., 10th Floor, 501 Grant St., Pittsburgh, PA 15219; (412) 261-2910.

### **High Strength Waste Treatment Options**

Peter Daley, Director of Research and Development, Chemical Waste Management, Inc., 150 W. 137th St., Riverdale, IL 60627; (312) 841-8360.

### **Where Do We Stand on Superfund?**

C. J. Touhill, Baker/TSA Division, Michael Baker, Jr., Inc., 4301 Dutch Ridge Rd., Beaver, PA 15009; (412) 495-7711.

### **The New CERCLA Regulations**

William Wallace, CH2M-Hill, 1500-114th Ave., S.E., Bellevue, WA, 98004; (206) 453-5000.

### **Acid Rain: What Does Science Tell Us?**

Thomas F. Lavery, Chairman, Vice President, Environmental Research & Technology, Inc., 696 Virginia Rd., Concord, MA 01742; (617) 369-8910. Richard D. Siegel, Vice Chairman, Senior Environmental Consultant, Environmental Research & Technology, Inc., 696 Virginia Rd., Concord, MA 01742; (617) 369-8910.

### **Chlorinated Organic Air Emissions**

Robert E. Kenson, Chairman, Met-Pro Corp., Systems Division, 160 Cassell Rd., Box 144, Harleysville, PA 19438; (215) 723-6751. Paul F. Fennely, Vice Chairman,

Environmental Research & Technology, Inc., 696 Virginia Rd., Concord, MA 01742; (617) 369-8910.

### **How Close to Refineries and Process Plants in Light of Today's Environmental Regulation**

J. A. Scher, Vice President, Resource Engineering, Inc., 3000 Richmond Ave., Houston, TX 77098; (713) 520-9900.

### **Managing Toxic Chemical Exposure at New/Existing Specialty Chemical Plants**

Ed Siskin, Chairman, Vice President, Stone & Webster Engineering Corp., One Penn Plaza, 250 West 34th St., New York, NY 10019; (212) 290-6252. Joseph J. Cramer, Vice Chairman, Stone & Webster Engineering Corp., P.O. Box 2325, Boston, MA 02107; (617) 589-2785.

### **Characterization and Control of Toxic Air Emissions at Uncontrolled Hazardous Waste Sites**

A. H. Wehe, 11117 Woodmont Dr., Raleigh, NC 27612; (919) 847-4372.

### **State Mandated Site Assessments Prior to Land**

**Transfer: Massachusetts Superlien and New Jersey's ECRA—A Vision of Things to Come**

William A. Duvell, Chairman, Senior Program Manager, ERT, Inc., 696 Virginia Rd., Concord, MA 01742; (617) 639-8910. B. Tod Delaney, Vice Chairman, Program Manager, CH2M-Hill, 169 Ramapo Valley Rd., Oakland, NJ 07436; (201) 337-9200.

### **Practical Aspects of Risk Management**

Ed Martin, Chairman, Hazardous Materials Control Research Institute, 9300 Columbia Blvd., Silver Spring, MD 20910; (301) 587-9390. B. T. Delaney, Vice Chairman, Program Manager, CH2M-Hill, 169 Ramapo Valley Rd., Oakland, NJ 07436; (201) 337-9200.

### **Treatment of Power Plant Wastewaters**

B. M. Kim, Chairman, General Electric Co., Corporate R&D, Schenectady, NY 12301; (518) 385-8824. Winston Chow, Vice Chairman, EPRI, 3412 Hillview Ave., P.O. Box 10412, Palo Alto, CA 94303; (415) 855-2868.

### **General Papers on Wastewater Treatment**

Harry E. Bostian, Chairman, Wastewater Research Division, US EPA, 26 West St. Clair St., Cincinnati, OH 45268; (513) 684-7613. Robert W. Coughlin, Vice Chairman, Department of Chemical Engineering, University of Connecticut, Storrs, CT 06268; (203) 486-4489.

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## **Conferences**

### **December 16-18, 1985 University of Wisconsin**

Leaking Underground Storage Tanks (LUST) will probably be the number one environmental problem for the remainder of the 1980's. The University of Wisconsin is offering a seminar which will deal with: Legal liabilities; How to detect tank failures; Ways to avoid future tank leakage problems. Contact Professor John T. Quigley, Department of Engineering Professional Development, University of Wisconsin, 432 North Lake Street, Madison, WI 53706.

### **January 16 & 17, 1986 ASME**

The American Society of Mechanical Engineers will sponsor a workshop on the regulation of underground storage tanks in Washington, DC. The meeting will focus on leak detection methods and technologies, drawing speakers from government and industry. The workshop is cosponsored by the American Institute of Chemical Engineers and the American Academy of Environmental Engineers. Contact ASME, 1825 K St. NW, Washington, DC 20006.

# WASHINGTON ENVIRONMENTAL NEWSLETTER

## **SUPERFUND — WHERE IT'S AT**

Technically the taxing authority under the superfund bill expired on September 30th. The program at EPA will continue on a smaller scale until the House passes its version of the bill and conferees reconcile differences with the Senate. That may be a long time coming, primarily because of the Senate's inclusion of an excise tax on all industries to finance the superfund program. Proponents of the tax argue that it is not intended to be a value added tax, while opponents claim that it is a VAT in everything but name. At the very end of debate on the bill, the Senate did adopt, by voice vote, a nonbinding resolution, sponsored by Senator Jesse Helms, stating that "the committee on conference. . . should report legislation containing a reliable financing mechanism for the superfund program which does not include the VAT." The House Ways and Means Committee has given no clear signal as to whether it will go along with the Senate's taxing proposal, maintain the current system of combining feedstock taxes and general revenues, or adopt a waste-end tax.

## **AMENDMENTS OF INTEREST**

Also of interest is the fact that the Senate adopted an amendment by Senator Frank Lautenberg which would mandate inventories of hazardous chemicals at each plant site, reporting of releases, and community right-to-know programs.

Another controversial section of the bill as reported out by the Environment and Public Works Committee, included a pilot program for victim's compensation. That section was *deleted* by a vote of 49 to 45.

## **INCLUSION OF R&D IN SUPERFUND**

In the House, an amendment was offered by Representative Torricelli (D-NJ) supported by Reps. Volkmer, Scheuer, Fuqua, Lujan and Schneider, that would authorize a program of research, development and demonstration for innovative or experimental treatment technologies for use in remedial actions. Basically, the amendment states that since the number of hazardous substance facilities requiring clean-up will increase substantially, EPA's practice of relying on removal and containment measures will not permanently reduce the risk of release of hazardous substances into the environment. The use of treatment technologies which permanently alter the composition of such wastes can provide significantly greater protection to the environment and public health. Stating that various regulatory factors often limit the ability of alternative and innovative treatment technologies to demonstrate the utility and cost-efficiency of technologies to reduce the toxicity, volume or mobility of hazardous wastes, the amendment goes on to propose a sustained program of research and development for alternative and innovative technologies to accomplish these objectives. In effect this amendment would change Title I of CERCLA by adding a new section (116) "Alternative or Innovative Treatment Technology Research, Evaluation and Demonstration Program."

EPA's Administrator would be charged to authorize and carry out the program and conduct a technology transfer program, including the development, collection, evaluation, coordination and dissemination of information related to alternative and innovative technologies. This program would be funded in the amount of no more than 25 million dollars for fiscal years '86, '87, '88, '89 and 1990. It is expected that the committee on Public Works will adopt this amendment when it is marked up during the week of October 18th. For more detailed information you may contact AICHe's Washington office.

## **OPPORTUNITIES FOR RETIRED CHEMICAL ENGINEERS IN COMMUNITY WORK**

The Washington office of AICHe has been working closely with EPA on its "Guidelines for Community Emergency Response." Since the technical knowledge of Chemical Engineer's is viewed as an integral part in this planning, there is an exceptional opportunity for Local Sections and retired Chemical Engineer's to participate and provide a real service to their communities. AICHe's Government Programs Steering Committee is working on a set of guidelines for community interaction, and retired AICHe members are urged to contact Marty Siegel at the Washington office.

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*This material was prepared by AICHe's Washington Representative Martin Siegel • Houston & Associates, Inc., Suite 804, 1901 L Street, N.W., Washington, D.C. 20036. Tel. (202) 223-0650*

# DATA COMPILATION TABLES OF PROPERTIES OF PURE COMPOUNDS

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# 1984 Survey of Research on Environmental Pollution—Its Sources, Fate, Effects, and Control

**A report of a 1984 survey of environmentally related research and/or design projects in progress at U.S. colleges and universities and industry.**

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## INTRODUCTION

The Environmental Research Committee of the AIChE, a joint committee of the AIChE Environmental Division and the AIChE Research Committee, conducted a survey in 1973 of environmentally related research and/or design projects in progress at U.S. colleges and universities. Because of the large number of chemical engineers involved with and concerned about environmental projects, the Environmental Research Committee in 1983 decided to update the earlier survey and extend it to include industrial research. Of interest was how the research effort had changed or shifted from 1973 and what were the perceived environmental research and design needs of the respondents. A revised version of the 1973 questionnaire was mailed in December 1984, with the responses collected until March 1985. This paper summarizes the results of the 1984 survey.

The complete report with appendices has been submitted to the U.S. Environmental Protection Agency to make it available through NTIS.

## SURVEY METHOD

A survey by mail was chosen in 1973 and again in 1984 because of the time and expense of any other survey method. It was recognized that mail surveys have two major problems. One is the lack of two-way communication and the other is a limited or low response. It was also recognized that other organizations had attempted to define environmental research needs (e.g., WPCF Wastewater Research Needs 1984), and that these efforts might inhibit the response. To help offset these problems, limited telephone follow-up was used for the 1984 survey.

The Committee completely redrafted the 1973 questionnaire to reflect the recent changes in the AIChE Environmental Division from specific media to cross-cutting programs. Emphasis was placed on research by chemical engineers or research applying chemical engineering principles. A section was added on research and design needs. A packet was mailed on December 5, 1984 to the Chemical Engineering Department Chairman at each of the 161 colleges and universities on the National AIChE mailing list. A response was requested by February 1, 1985. Each packet contained a cover letter explaining the purpose of the survey, a form for the university or college contact person, and a number of research project forms.

Each investigator was asked to classify his research project using 12 categories.

A similar packet with the same response date was mailed to 230 companies. The difference was that the packet mailed to industry separated the research and design needs from the project form. This was done to encourage practicing engineers to submit their perception of the research and design needs in environmental pollution control when they could not, for one reason or another, submit project information. The list of companies was compiled from *C&E News'* top chemical companies and a list used in 1982 by the National AIChE office for a hazardous waste study. The packet was mailed to either the chief executive officer, president, vice-president, an environmental affairs officer, or an AIChE Research Committee contact person.

Before the survey mailings, a packet was sent to three universities and one company to test the questionnaire forms for any unforeseen difficulties. Each university had to be contacted by telephone whereas the company responded within two weeks with completed forms. No problems with the forms were uncovered. This test mailing, however, did show the importance of personal contact. The industrial company contact had been aware of and supportive of the project.

A packet containing the industrial questionnaire and a letter of explanation was sent to the American Petroleum Institute, National Agricultural Chemist's Association, National Petroleum Refiners Association, Chemical Manufacturer's Association, and the Dyes Environmental and Toxicological Organization. The purpose was to increase the industrial response by soliciting their support in the event that they received an inquiry from one of their members.

## SURVEY RESPONSE AND DISCUSSION

The colleges and universities responding to the 1984 survey are shown in Table 1 along with their responses. Follow-up telephone calls were made to 15 universities that received the forms, but who failed to respond by February 1, 1985. Of these, only one could complete the forms within the allowed time period. This gave a total of 58 schools responding out of the 161 schools receiving the questionnaire. From these 58 schools, 48 were engaged in 150 research projects. The 1973 survey questionnaire was mailed to 130 schools with 75 responding. Of these 75,

TABLE 1. UNIVERSITIES RESPONDING TO THE 1984 SURVEY OF RESEARCH ON ENVIRONMENTAL POLLUTION — ITS SOURCES, FATE, EFFECTS AND CONTROL

University	Response
University of Akron	1 Project
University of Alabama	1 Project
University of Alberta	1 Project
University of Arizona	2 Projects
Auburn University	No Current Projects
University of Calgary	1 Project
University of California/Berkeley	3 Projects
California Institute of Technology	No Current Projects
Clemson University	No Current Projects
Cleveland State University	2 Projects
University of Colorado	No Current Projects
Colorado State University	18 Projects
University of Connecticut	1 Project
Cornell University	3 Projects
University of Florida	3 Projects
Georgia Institute of Technology	2 Projects
University of Idaho	1 Project
University of Iowa	1 Project
Kansas State University	1 Project
University of Kentucky	6 Projects
Lafayette College	No Current Projects
Laval University	1 Project
Louisiana State University	11 Projects
Louisville Speed Scientific School	3 Projects
McGill University	4 Projects
McMaster University	4 Projects
University of Massachusetts	6 Projects
Michigan State University	1 Project
Michigan Technological Univ.	7 Project
Mississippi State University	No Current Projects
University of Missouri/Columbia	4 Projects
Montana State University	1 Project
University of Nebraska	No Current Projects
University of New Brunswick	1 Project
New Jersey Inst. of Tech.	6 Projects
University of Notre Dame	1 Project
Ohio State University	6 Projects
Ohio University	2 Projects
Oklahoma State University	3 Projects
The Inst. of Paper Chemistry	1 Project
Pennsylvania State University	2 Projects
University of Pittsburgh	1 Project
Princeton University	2 Projects
Purdue University	8 Projects
University of Rochester	2 Projects
Rose-Hulman Inst. of Technology	No Current Projects
Rutgers-The State University	10 Projects
Syracuse University	Will Respond Later
Texas Tech University	4 Projects
University of Toledo	2 Projects
University of Toronto	3 Projects
University of Tulsa	1 Project
University of Utah	1 Project
University of Washington/Seattle	1 Project
Washington State University/Pullman	1 Project
Washington University/St. Louis	No Current Projects
Wayne State University	2 Projects
University of Western Ontario	1 Project

only 44 had significant project activity with a total of 361 projects.

Although the number of schools responding with project information is about the same, there are significant differences between the above results for 1973 and 1984. The most obvious is the number of projects. The number of active environmentally related research projects reported in 1973 was more than twice the number reported in 1984. This decline in the number of projects could be attributed to sampling bias, a maturing of the environmental research

TABLE 2. COMPANIES RESPONDING TO THE 1984 SURVEY OF RESEARCH ON ENVIRONMENTAL POLLUTION — ITS SOURCES, FATE, EFFECTS AND CONTROL

Industry	Response
Air Products & Chemicals, Inc.	Research & Design Needs
Allied Chemical Company	Research & Design Needs
American Brands	Declined to Participate
American Home Products Corp.	Declined to Participate
Amoco	Research & Design Needs
ASARCO, Inc.	Research & Design Needs
Badgers Engineers Inc.	1 Project
The Boeing Company	6 Projects
Bristol-Myers Company	No Current Projects
Carus Chemical	2 Projects
Champion International Corporation	No Current Projects
Cosden Oil & Chemical Company	No Current Projects
Crompton & Knowles	Research & Design Needs
Dow Chemical Company	Research & Design Needs
Dundee Cement Company	No Research Activity
E. I. DuPont de Nemours & Company	Declined to Participate
El Paso Natural Gas Company	No Research Activity
Emhart Corporation	No Current Projects
Ethyl Corporation	No Current Projects
Fluor Power Service Corporation	6 Projects
Gas Research Institute	Research & Design Needs
W. R. Grace & Co.	Declined to Participate
Great Lakes Chemical Corporation	Research & Design Needs
Hercules Incorporated	1 Project
Inland Steel Company	6 Projects
Marathon Petroleum	No Current Projects
Mobil Oil Company (Res. & Dev.)	Research & Design Needs
Monsanto Company	4 Projects
Occidental Chemical Corporation	2 Projects
Olin Corporation	2 Projects
Ralph M. Parsons Corporation	No Current Projects
Phillips Chemical Company	No Research Activity
Schering-Plough Company	Research & Design Needs
Shell Development Company	3 Projects
Stauffer Chemical Co.	No Current Projects
Texaco	Telephone Response
Waste Management, Inc.	2 Projects
Zimpro Inc.	Declined to Participate

effort, or limited availability of research monies from all sources. For example, the impact of newly enacted pollution control regulations in the early 1970's was significant in the 1973 survey. In responding to the need to limit emissions and effluents, industry sponsored a number of short term structured research projects. That short term demand is no longer evident in 1984.

Another significant difference is the population of schools responding. Only 14 of the 44 schools with projects in 1973 responded with projects in 1984. No Canadian schools responded in 1973 while 6 responded with projects in 1984. This could reflect a shift in interest or personnel, or both.

Of the 230 companies contacted, 38 companies provided a written response with 11 of them involved in 33 research projects as shown in Table 2. The distribution of the industrial and university response by project category is shown in Table 3. A number of the packets (16) mailed to industry were returned unopened. In each case the CEO prior to 1984 had left the company. The first 6 returned like this were remailed to the current CEO; still, no response was received. The low response from industry can be attributed to a number of factors: (1) poor economic times; (2) lack of interest or understanding; (3) tired of so many questionnaires; (4) the "plain brown envelope" used to mail the packet; (5) the questionnaires did not reach the right peo-

TABLE 3. TOTAL NUMBER OF RESEARCH PROJECTS BY PROJECT CATEGORIES

Project Category	Industry (no. projects)	University (no. projects)	Total	%
1. Pollution source identification/characterization	1	29	30	16.4
2. Water, air, thermal, and noise pollution control technologies	15	45	60	32.8
3. Solid/hazardous waste handling, treatment, storage and disposal	6	10	16	8.7
4. Waste recycling/reuse	4	6	10	5.4
5. Manufacturing process changes to eliminate/reduce waste discharges	1	5	6	3.3
6. Economic impacts and cost analyses of pollution/pollution control	0	3	3	1.6
7. Legal and policy research related to technological options	1	1	2	1.1
8. Pollution control strategies (e.g. in different media and different environments)	0	7	7	3.8
9. Chemical and biological effects and interactions/ environmental modeling	0	27	27	14.7
10. Detection, measurement and analytical methods	1	10	11	6.0
11. Global environmental problems such as the CO <sub>2</sub> greenhouse effect or acid rain	0	2	2	1.1
12. Other	4	5	9	4.9
			183	99.8%

ple; (6) no environmental research projects; (7) a belief that there are no environmental research needs; (8) insufficient time to respond or respond fully, and many others. Some of these reasons are speculation, some from the responses, and some from telephone contact. Most often, it was a corporate policy not to participate in these types of activities.

From the information shown in Table 3 pollution control technology is receiving the most effort with about 30% of the projects. No thermal or noise pollution control projects were reported. The split between water and air projects was about 2:1. This is the same ratio of effort reported in 1973. Solid waste projects were about 9% of the effort in the 1973 survey results and 9% in 1984. Some investigators gave both water pollution control technology and solid waste treatment as the primary objective of their research, thus, there is some crossover between the water projects and the solid waste projects. Although only one category was used in compiling the statistics, an attempt was made to choose the category most closely aligned with the project based on the information provided.

The next major category of effort was Pollution Source Identification/Characterization with about 16%. This was not identified in the 1973 survey.

Category 9 — Chemical and Biological Effects and Interactions/Environmental Modeling, is receiving the third largest effort with about 15%. The modeling aspect of this category is in agreement with the third major effort identified in the 1973 survey, while in 1973 chemical and biological effects were among those receiving the least effort. This shift is in agreement with the change in emphasis to specific pollutants and the generally held belief that there may not be a threshold for carcinogenic effects.

If Category 10 — Detection, Measurement and Analytical Methods, is combined with Category 12 — Other, then about 11% of the 1984 effort is in this area. The Other category is mainly physical/chemical property data. In the 1973 survey, the topics of these two categories were considered together. With this combination the ranking of this effort is in agreement with the 1973 results.

In 1973, legal, economic, and health aspects were receiving the least emphasis. In 1984, this still holds true for the legal and economic categories (6 and 7). This is somewhat surprising based on the emphasis placed on economics in chemical engineering curricula. However, this may be due to the perspective of those completing the forms rather than an accurate reflection of budgeted efforts.

Inadvertently, the project form mailed to the universities was missing Category 11 — Global Environmental Problems such as the CO<sub>2</sub> Greenhouse Effect or Acid Rain. Even with this omission it was still surprising that only one project was identified as having its major objective directly dealing with the acid rain problem. Certainly, those projects involved in the control of SO<sub>x</sub> and NO<sub>x</sub> are related to acid rain, even if the control of acid rain was not their primary objective. It could be that either acid rain research efforts do not involve chemical engineers and chemical engineering principles, those involved in this research did not respond to the questionnaire, or very little is being done on this topic. Most probably, it was a lack of response.

The environmental process design needs and the environmental research needs identified and ranked first, second and third by the 1984 survey respondents are summarized in Table 4. In the areas of most reported activity (categories 2, 3, and 9) industry respondents identified as many or more design needs as did the university respondents. University respondents identified far more research needs than did industry respondents in most categories. The needs were grouped according to the categories used for projects. This was a subjective judgment of the Committee and may not accurately reflect the choice that the respondent would have made. In most cases the needs were categorized according to the respondent's primary and secondary categories for his project. The one deviation from this was that needs dealing with models were classed in Category 9 — Chemical and Biological Effects and Interactions/Environmental Modeling.

The ranking given by the percentage response for the top four research and design needs shown in Table 4 are: (1) Category 2 — Pollution Control Technology, 33%; (2) Category 9 — Chemical and Biological Effects/Modeling, 22%; (3) Category 10 — Measurement Methods, 15%, and (4) Category 3 — Solid Waste, 11%. This ranking is in agreement with that based on the percentage of the project activity efforts reported in the 1973 and 1984 surveys. Thus, the relative importance and interest in these categories has remained about the same over the past decade.

No industrial respondent identified a need in Category 6 — Economic Impacts and Cost Analyses of Pollution/Pollution Control. This resulted in the lowest ranking for economic studies, which was preceded by Category 8 — Strategies, Category 1 — Pollution Source, Category 11 — Global, and Category 7 — Legal. All five of these categories combined had less than 6% of the identified needs.

TABLE 4. SUMMARY OF THE CATEGORIES OF RESEARCH AND DESIGN NEEDS AS PERCEIVED BY INDUSTRIAL AND UNIVERSITY RESPONDENTS

Category	Rank*:	Industrial			University			Total							
		Research	Design		Research	Design		No.	%						
1. Pollution Source Identification/Characterization		-	-	2	-	-	-	5	1.1						
2. Water, Air, Thermal and Noise Pollution Control Technologies		11	10	6	18	17	13	25	11	9	147	33.0			
3. Solid/Hazardous Waste Handling, Treatment, Storage & Disposal		1	2	3	5	6	5	2	6	5	49	11.0			
4. Waste Recycling/Reuse		1	1	1	1	1	-	2	3	-	12	2.7			
5. Manufacturing Process Changes to Eliminate/Reduce Waste Discharge		1	5	-	5	3	1	2	5	4	35	7.8			
6. Economic Impacts and Cost Analyses of Pollution/Pollution Control		-	-	-	-	-	-	-	-	-	3	0.7			
7. Legal and Policy Research Related to Technological Options		-	3	2	-	-	-	1	1	2	-	-	9	2.0	
8. Pollution Control Strategies (e.g. diff. media and diff. environments)		-	1	-	-	-	-	-	3	-	-	-	5	1.1	
9. Chemical and Biological Effects and Interactions/Environmental Modeling		5	2	2	-	-	2	42	22	13	4	3	1	96	21.5
10. Detection, Measurement and Analytical Methods		1	1	4	-	1	-	16	16	12	6	7	2	66	14.8
11. Global Environmental Problems (CO <sub>2</sub> Greenhouse Effect or Acid Rain)		-	-	1	-	-	1	-	-	5	-	-	-	7	1.6
12. Other (physical properties, database, training)		-	-	-	2	2	-	4	1	2	1	-	-	12	2.7
														446	99.5

\*Respondents ranked their top three research and design needs.

A comparison of the active projects with the identified research and design needs indicates that the match between project effort and perceived needs is fairly good for most of the categories as shown in Figure 1. Notable exceptions are in Categories 1, 9, and 10. In Category 1, the project effort far exceeds the perceived needs. This suggests that the major sources of pollution have either been addressed and characterized or that they are in progress. A greater effort is suggested for Categories 9 and 10 (effects, modeling, and measurement) which is consistent with the definition of ultimate impact of emissions and effluents on the environment in general and people specifically.

The industrial participants were asked to provide their opinion of how the total environmental research effort should be divided among various categories and pollutant media. Their perceptions are shown in Tables 5 and 6. The greatest efforts are perceived to be transport and fate (16%), health effects (18%), and pollutant control technology (23%). Chemical engineers are expected to provide significant research efforts in transport and fate (17%) and pollutant control technology (32%). Our expected research effort in health effects (4%) ranks near the bottom. The distribution of effort by pollutant medium has a perceived need of almost one-to-one for the major environmental acts. If these concerns are grouped by medium, then the overall effort needed is perceived to be 4:1:1 for water, air, and solid waste, respectively. Although drinking water cleanup is ranked lower than the others, water quality is definitely the top concern of the respondents.

Table 7 contains a comparison of the 1973 reported project funding for universities with the university reported project funding for 1984. The total project funding of \$16 million is the same for both surveys. When the number of active projects reported in each survey is considered with the inflation rate, the average cost for an environmental research project has remained about the same (in 1984 dollars, about \$100K/project).

TABLE 5. INDUSTRIAL PERCEPTION OF THE DISTRIBUTION OF ENVIRONMENTAL RESEARCH EFFORTS

Category	Percent of Research Effort	
	Total	By Ch.E.'s
A. Health effect of pollutants	18	4
B. Environmental Impacts	10	5
C. Mechanisms of pollutant formation	5	9
D. Environmental transport and fate of pollutants	16	17
E. Measurement of pollutants released from industrial processes	7	11
F. Research on measurement/analytical methodology	8	3
G. Pollutant control technology	23	32
H. Environmental reclamation and/or correction of past improper practices	9	13
O. Other	4	6

TABLE 6. INDUSTRIAL PERCEPTION OF THE DESIRED DISTRIBUTION OF RESEARCH EFFORT BY POLLUTANT MEDIUM

Category	Overall Effort, %
A. Air (Clean Air Act)	23
B. Surface Water (Clean Water Act)	18
C. Groundwater	23
D. Drinking water cleanup (SDWA)	11
E. Solid waste (RCRA, CERCLA)	20
F. Intermedia (i.e., interaction between air and water pollution)	5

The breakdown of the funding sources for the 1984 survey was: \$12 million from government agencies, \$2 mil-

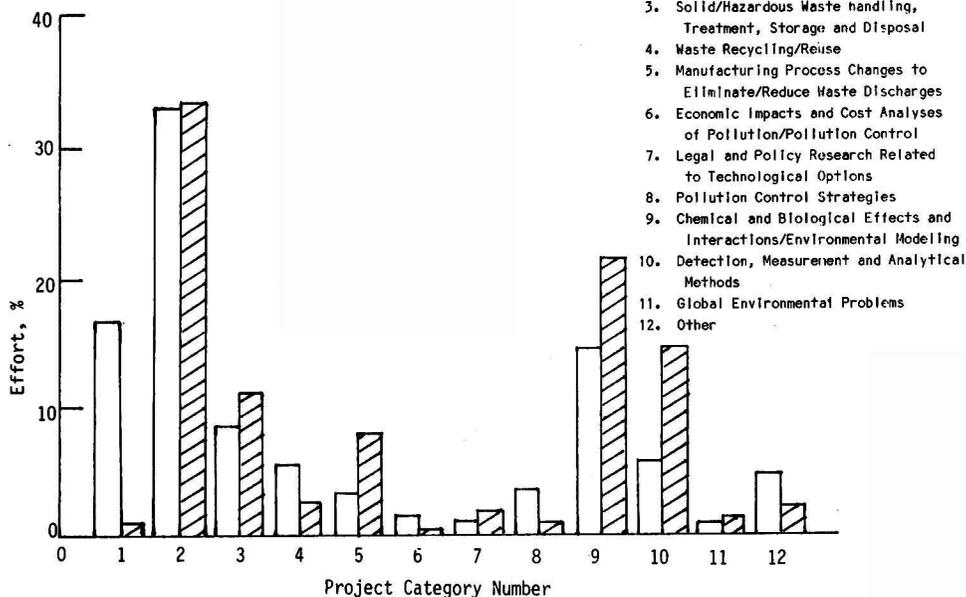


Figure 1. Percentage distribution of effort for active projects and perceived needs by project category.

lion from industrial sources, \$1 million from the universities, and \$1 million from other sources. Of the \$12 million from government agencies, \$4 million was from EPA. Thus, EPA is providing 30% of the funds from government sources for environmental research reported in the 1984 survey, or 25% of the total reported funds.

## CONCLUSIONS

Based on the project information received, the identified research and design needs submitted, and observations made during this study, several conclusions have been made.

- There has been a dramatic decrease in environmental research activity involving chemical engineering principles over the past decade as measured by the number of active projects reported in the two surveys.
- Research on pollution control technology is the area with the greatest perceived need and the greatest current effort.
- Water pollution control projects outnumber air pollution control projects by a factor of 2:1.
- The lowest emphasis is on legal and economic problems.
- Greater emphasis should be placed on chemical and biological effects and interactions, environmental modeling, pollutant detection, measurement and analytical methods.

If future surveys of this type are made, it is recommended that a special effort be made to obtain a larger response for environmental research and design needs from those active in plant design, operation, and maintenance. The people involved in these areas may not be involved in research and may not be aware of the survey without a special effort. In addition, the data gathering approach for this

type of data could be improved by starting from existing databases (e.g., EPA, DOE, DOD, and SSIE) of ongoing research and then use these data to select candidate schools and companies for the follow-up survey. This would result in the survey being a validating tool for the data gleaned from the funding agency lists.

## LIMITATIONS

The use of the results of the 1984 Environmental Research Survey presented in this paper and the complete report should be made with caution. The low project response from industry makes the use of this information qualitative at best. Many schools and industries known to be engaged in environmental research failed to respond; therefore, their input is missing. The groupings of the research and design needs were made by the Committee and may not accurately reflect the respondent's choice or intention.

## ACKNOWLEDGMENTS

This survey was conducted with the advice and assistance of the AIChE Environmental Research Committee. The members of this Committee from the AIChE Environmental Division were: William J. Lacy, J. M. Schroy, Paul Shapiro, David G. Stephan, and Leo Weitzman. Members from AIChE's Research Committee were Atly Jefcoat and Henry Shaw. The survey received financial and/or in-kind support from the Environmental Division of AIChE, the Research Committee of AIChE, The University of Alabama, and the U.S. Environmental Protection Agency's Office for Research and Development (under Grant No. R811632-01-0).

TABLE 7. COMPARISON OF 1973 REPORTED FUNDING LEVELS WITH 1984 REPORTED FUNDING LEVELS FOR UNIVERSITY PROJECTS

1973 University Project Category		Funding	1984 University Project Category		Funding
I. Water Pollution	-A-Measurement methods	\$ 694,473	1. Pollution source identification/ characterization		\$ 3,168,345
	B-Abatement & controls	2,914,257	2. Water, air, thermal, and noise pollution control technologies		3,844,142
	C-Legal and economic aspects	561,000	3. Solid/hazardous waste handling, treatment, storage and disposal		1,014,961
	D-Predictive modeling	2,908,011	4. Waste recycling/reuse		230,246
	E-Effect on health and vegetation	952,449	5. Manufacturing process changes to eliminate/reduce waste discharges		1,016,500
II. Air Pollution	F-Misc. (surveys, training, materials studies)	2,113,300	6. Economic impacts and cost analyses of pollution/pollution control		1,346,000
	-A-Measurement methods	1,000,700	7. Legal and policy research related to technological options		18,000
	B-Abatement & controls	1,102,245	8. Pollution control strategies (e.g. in different media and different environments)		842,714
	C-Legal and economic aspects	11,000	9. Chemical and biological effects and interactions/environmental modeling		3,227,231
	D-Predictive modeling	79,850	10. Detection, measurement and analytical methods		1,052,598
III. Solids Waste	E-Effect on health and vegetation	101,800	11. Global environmental problems such as the CO <sub>2</sub> greenhouse effect or acid rain		—
	F-Misc. (surveys, training, materials studies)	396,900	12. Other (phys. properties, databases, training)		673,359
	-A-Measurement methods	1,000			
	B-Abatement & controls	501,270			
	C-Legal and economic aspects	—			
IV. Noise Pollution	D-Predictive modeling	81,500			
	E-Effect on health and vegetation	274,000			
V. Graduate Training		170,000			
VI. Air/Water/Solids Pollution Interaction		351,000			
		1,583,000			
TOTAL		\$ 15,797,755	TOTAL		\$ 16,434,096



Irvin A. (Atty) Jefcoat is serving on the Chemical Engineering faculty at The University of Alabama. In addition, he is the Staff Engineer for the University's Environmental Institute for Waste Management Studies and one of the principal investigators for the University's Hazardous Materials Management and Resource Recovery Program. His principal research interests are industrial environmental problems, synfuels, and alternate chemical feedstocks. He is engaged in specific research on interphase transport of pollutants, formation of toxicological compounds from high temperature processes, and the use of lignins as an alternate chemical feedstock.

He received his Ph.D. and Master's in chemical engineering from Clemson University and is a registered Professional Engineer in North Carolina and Tennessee.

# Combined SO<sub>2</sub>/NO<sub>x</sub> Removal from Flue Gas

## Detailed discussion of a new regenerative fluidized-bed process developed by the Pittsburgh Energy Technology Center.

James T. Yeh, Richard J. Demski, Joseph P. Strakey, and James I. Joubert,  
Dept. of Energy, Pittsburgh Energy Technology Center, Pittsburgh, Pa. 15236

Development of a regenerative fluidized-bed process for simultaneous removal of SO<sub>2</sub> and NO<sub>x</sub> from flue gas has been underway at the Pittsburgh Energy Technology Center (PETC) since the late 1960's. In 1970, McCrea *et al.* [1] reported on the bench-scale evaluation of SO<sub>2</sub> removal using copper-impregnated alumina spheres and presented preliminary design criteria for a process to be used to treat flue gases from a 1000-MW utility boiler burning a 3%-sulfur coal. A copper-impregnated UOP alumina sorbent, containing 6.3 wt.% Cu, was tested over 200 cycles of SO<sub>2</sub> absorption and regeneration with CH<sub>4</sub> in a fixed-bed bench-scale reactor. No deterioration of the physical or chemical properties of the sorbent was observed during these tests.

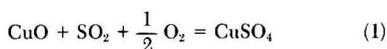
Fluidized-bed testing (at PETC) of the same sorbent material was begun in 1975 using a 6-inch (15.2-cm)-diameter reactor, and the initial results were reported by Strakey *et al.* [2]. The tests were conducted with the combustion products of natural gas, spiked with SO<sub>2</sub>. The SO<sub>2</sub> removal was measured as a function of solids feed rate, bed height (18 inches and 36 inches; 0.457 m and 0.914 m), and bed temperature (662°F and 750°F or 350°C and 400°C); 75 absorption-regeneration cycles were completed. During several cycles, ammonia was injected for the simultaneous removal of NO<sub>x</sub>.

The results of this study were sufficiently promising to merit continued development of the process. In addition to a continuing evaluation of repeated sorption/regeneration cycles on sorbent activity, the test program included the following: a determination of the effect of NH<sub>3</sub>/NO<sub>x</sub> mole ratio on simultaneous removal of SO<sub>2</sub> and NO<sub>x</sub>; measurement of ammonia "slip" (unreacted ammonia); *in situ* measurements of sorbent attrition occurring in the fluidized bed; and an evaluation of the effect of fly ash addition on reactor performance. The results of these successful tests were reported at the 1982 Summer National Meeting of the AIChE in Cleveland, Ohio [3].

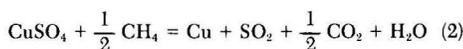
Based on the results of the previous research, a 3 ft 4 inch × 4 ft 0 inch cross-section × 12 ft 0 inch (1.016 m × 1.219 m cross-section × 3.658 m) high fluidized-bed absorber was designed, fabricated, and installed in a 500 lb/hr (2.268 kg/h) pulverized-coal-fired combustion test facility. A 2 ft 6 inch (0.762 m) diameter × 26 ft 0 inch (0.66 m) high regenerator was also constructed to regenerate the spent sorbent from the absorber. The results of tests conducted in this facility are discussed in this report.

### DESCRIPTION OF PROCESS

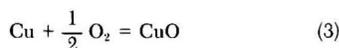
The SO<sub>2</sub> and O<sub>2</sub> in the flue gas react with copper oxide to form the sulfate:



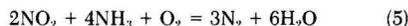
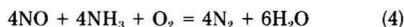
The spent sorbent can be regenerated with methane or other reducing gases, such as H<sub>2</sub> and CO. With methane, the overall reaction is expressed by the following



When the regenerated sorbent is exposed to flue gas, the elemental copper is converted to the oxide:



The reaction of NH<sub>3</sub> with NO<sub>x</sub> in the fluidized bed is catalyzed by both CuSO<sub>4</sub> and CuO, the former being more effective:



Other NO<sub>x</sub> reduction reactions not involving oxygen are also believed to occur.

The Shell copper oxide process is based on similar chemistry but uses a cyclic fixed-bed contactor in which the supported sorbent is contained in parallel trays [4, 5, 6]. The process is licensed by the UOP Process Division in this country and is referred to as the UOP/Shell Process.

The fluidized-bed design has several significant advantages over a fixed-bed design:

- No valve problems. No large-diameter valves are needed to isolate the absorber from the regenerator as in the fixed-bed design.
- Constant regenerator off-gas. Fixed beds produce a cyclic feed to the sulfur recovery unit.
- Fly ash passes through the fluidized bed, avoiding plugging that can occur in fixed beds.

The main potential disadvantages are the following:

- Higher pressure drop than in the parallel passage reactor.
- Potential for attrition of the sorbent.

### SORBENT PREPARATION

The sorbent used in this test program was in the form of 1/16-inch (0.16-cm)-diameter copper-impregnated spheres of gamma alumina purchased from UOP. The spheres were immersed in a 22.5-wt.% solution of copper nitrate trihydrate for a period of about 1/2 hour. After the excess solution was drained, the sorbent was placed in an oven and heated to 300°F (149°C) and kept at this temperature for about 16 hours. The sorbent temperature was then raised to 1200°F (650°C) and held at this temperature for six hours for calcination under a flow of nitrogen. The resulting copper concentration was 5.1 wt.%.

## DESCRIPTION OF TEST FACILITY

### Combustion Test Facility

The 500 lb/hr (226.8 kg/h) combustion test facility is shown schematically in Figure 1. The furnace was designed to simulate the performance of an industrial steam generator. The furnace walls are refractory-lined and water-cooled. The unit is 7-ft (2.13-m)-wide, 5-ft (1.52-m)-deep, and 12-ft (3.66-m)-high, and has a volumetric heat-liberation rate of about 16,000 Btu/hr-ft<sup>3</sup> (165,662 W/m<sup>3</sup>) at a thermal input of 6.5 million Btu/hr (1.9 × 10<sup>6</sup> W). The flue gas flow rate is approximately 1300 scfm (1 atm., 32°F) or 0.613 cubic meter per minute [1.01 (10<sup>6</sup> Pa, 0°C)].

Coal is charged to the hopper, pulverized to a size of 70% minus 200 mesh, and then conveyed by the primary air into a recycle coal loop, where intimate mixing of coal and air occurs. Four adjustable exit tubes are connected to the recycle loop; these convey the primary air-coal mixture to each of the four burners. Secondary air at 600°F (316°C) is fed through adjustable swirl vanes surrounding each burner. The flue gas exits the furnace at about 2000°F (1093°C), passes through a convective heat transfer section, enters the fluidized-bed absorber, passes through a recuperative air preheater where the secondary air is preheated, and then exits the system through a baghouse, an induced-draft fan, and a stack.

A pictorial view of the fluidized-bed absorber is shown in Figure 2. Sorbent from the storage hopper is fed into the side of the absorber via a side-entry rotary airlock feeder. The sorbent hopper is set on four load cells that are used to calculate a feed rate by the loss in weight per unit of time. The bed height was controlled by gravity flow of the sorbent through the side of the absorber at either 18 inches (0.457 m) or 36 inches (0.914 m) above the distributor plate. The removal rate through the original openings became too slow (bed height began increasing) at the higher sorbent feed rates, so a 3-inch (7.6-cm)-diameter pipe was installed at each level to maintain uniform bed heights at feed rates as high as 3000 lb/hr (1360.8 kg/h). The distributor plate contains 115 bubble caps (see Figure 3) spaced on 4-inch (10.1-cm) centers.

The sorbent regenerator was an alonized vessel 2.5 ft (0.762 m) in diameter by 26 ft (7.92 m) high. The sorbent was regenerated batchwise in a static bed after each absorption test. The sorbent was preheated with nitrogen to about 572°F (300°C) prior to switching to natural gas or natural gas/hydrogen mixtures for removal of sulfur from the sorbent. The operating temperature of the regenerator was about 788°F (420°C). The regenerated sorbent contains about 1 weight-percent residual sulfur.

### Test Procedure

Tests were carried out by first warming the combustor while burning natural gas. After the combustor had been warmed up, coal combustion was initiated. When the flue gas temperature reached the desired level, the SO<sub>2</sub>/NO<sub>x</sub>

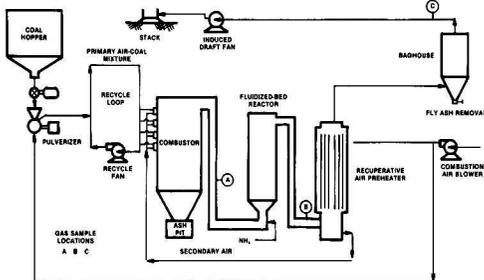


Figure 1. Simplified flowsheet of 500-lb/hr (226.8 kg/hr) combustion test facility.

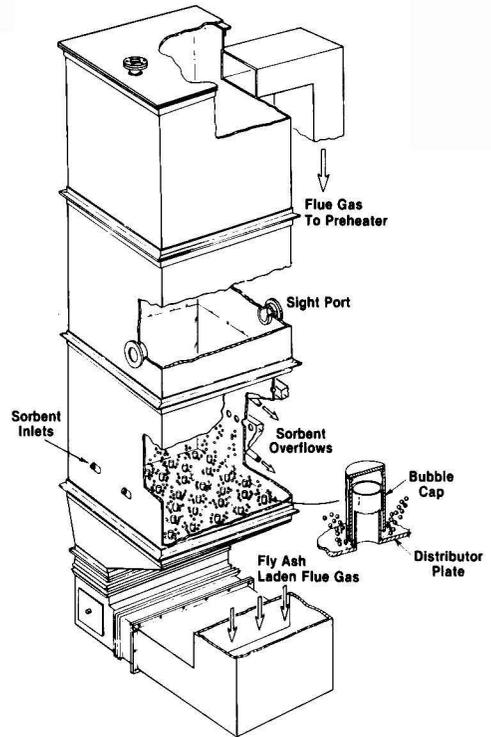


Figure 2. Fluidized-bed absorber (1.1016 m × 1.219 m × 3.658 m).

removal test was begun by introducing the sorbent into the fluidized-bed reactor and establishing the feed rate required for a certain level of SO<sub>2</sub> removal. The NH<sub>3</sub> injection rate was then adjusted to achieve the desired level of NO<sub>x</sub> removal. A typical test normally required about 10 hours of operation, including 1 to 3 hours of actual sorbent feed. At the end of a test, the sorbent flow into and the

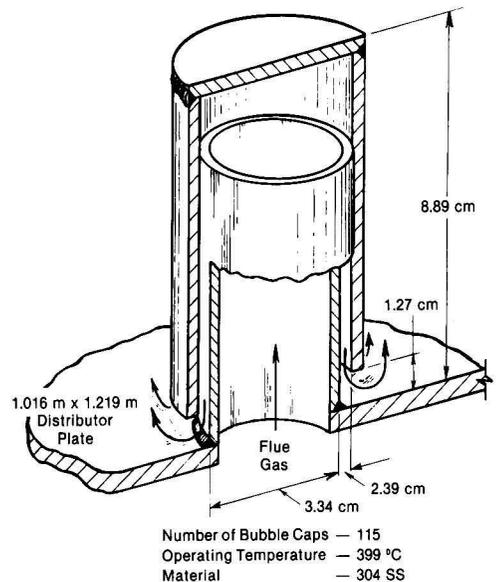


Figure 3. Bubble cap.

sorbent flow out of the reactor were terminated simultaneously.

The coal used in this series of tests was a Pittsburgh seam coal from West Virginia containing about 3% sulfur. The combustor was operated with 20% excess air.

## RESULTS

The original objectives of the test program were the following: 1) determine the required sorbent flow rates to achieve SO<sub>2</sub> removal efficiencies ranging from 70% to 90% while burning 3%-sulfur coal (which results in nominal uncontrolled SO<sub>2</sub> and NO<sub>x</sub> levels of 2300 ppm by volume and 500 ppm by volume, respectively); 2) determine the required NH<sub>3</sub> injection rates to achieve NO<sub>x</sub> removal efficiencies ranging from 40% to 90%; and 3) conduct similar series of tests at higher inlet SO<sub>2</sub> levels (2500 and 3000 ppm by volume) by injecting SO<sub>2</sub> into the combustion gases, and at higher NO<sub>x</sub> levels (800 and 1000 ppm by volume) by oxidizing NH<sub>3</sub> to NO<sub>x</sub> in the combustor. It was anticipated that the bulk of the tests would be conducted using a 36-inch (0.914-m)-deep bed at ≈750°F (399°C); several tests were planned at lower bed temperatures to simulate load-following conditions. Six tests were planned using an 18-inch (0.457-m)-deep bed operating at 750°F (399°C).

Results of the SO<sub>2</sub>/NO<sub>x</sub> removal tests conducted are given in Tables 1-3. Several difficulties were encountered

in attempting to carry out the test schedule exactly as planned. Although initial tests were to be conducted in a 36-inch (0.914-m)-deep bed, the openings in the reactor wall [at the 36-inch (0.914-m) level] did not provide adequate flow of sorbent from the reactor to maintain the bed level at 36 inches (0.914 m); as a result, a number of tests (Table 1) were actually conducted at bed depths of about 46 inches (1.17 m) (estimated from bed inventory and visual observation) before the problem was corrected. Controlling the bed temperature at 750°F (399°C) proved more difficult than originally anticipated, resulting in data being obtained over a broader temperature range than planned.

## SO<sub>2</sub> Absorption

Sulfur dioxide removal efficiencies obtained under all conditions are plotted in Figure 4 as a function of the Cu/S mole ratio, which is defined as moles of available Cu (i.e., Cu not combined with S) in the sorbent feed divided by moles of S in the inlet SO<sub>2</sub>. The data obtained using the 46-inch (1.17-m)-deep and the 36-inch (0.914-m)-deep beds were separated into two temperature ranges in an attempt to discern temperature effects on SO<sub>2</sub> removal efficiencies.

Figure 4 indicates, as expected, that, as bed depth increases, the Cu/S ratio required to achieve a given SO<sub>2</sub> removal decreases. There is no discernible effect of temper-

TABLE 1. RESULTS OF FLUIDIZED BED-COPPER OXIDE PROCESS TESTS, 46-INCH (1.17-M)-DEEP BED

Test No.	3	4	5	6	7	8	9	26	27	28
SO <sub>2</sub> Removal, %	79	71	90	91	70	81	91	90	90	90
NO <sub>x</sub> Removal, %	92	92	93	94	93	93	93	46	77	92
Inlet SO <sub>2</sub> (Dry), ppm by vol.	2280	2280	2354	2680	2680	2680	3100	2100	2100	2100
Inlet NO <sub>x</sub> (Dry), ppm by vol.	520	520	520	500	520	520	510	650	650	650
Bed Temperature, °F	840	860	750	750	810	750	760	790	790	790
Sorbent Feed, lb/hr	820	640	1475	1882	775	932	2321	1681	1681	1681
lb Sorbent/1000 scf	12.4	9.6	21.7	26.48	10.7	12.83	33.7	22.4	22.4	22.4
Available Cu, %	3.0	3.0	2.8	3.0	3.3	3.3	2.5	3.0	3.0	3.0
Cu/S Mole Ratio	0.99	0.78	1.57	1.8	0.8	0.96	1.71	1.86	1.86	1.86
Mole SO <sub>2</sub> Removed per Mole Available Cu	0.795	0.92	0.57	0.506	0.876	0.826	0.532	0.48	0.48	0.48
NH <sub>3</sub> /NO <sub>x</sub> Mole Ratio	0.98	0.98	1.0	0.87	0.92	0.92	0.69	0.26	0.50	0.66
Bed Inventory, lb (Measured after test)	1353	1353	1403	1413	1406	1406	1534	1291	1291	1291
Pressure Drop, inches W.C.	26	26	27	27	27	27	27	26	26	26
Superficial Velocity, ft/s	3.4	3.4	3.5	3.6	3.9	3.7	3.6	4.0	4.0	4.0

°C = (°F-32)/1.8, kg/h = 2.205 lb/hr, m<sup>3</sup> = 35.31 ft<sup>3</sup>, Pa = 0.00402 inch W.C., kg = 2.205 lb, m/s = 3.281 ft/sec.

TABLE 2. RESULTS OF FLUIDIZED-BED COPPER OXIDE PROCESS TESTS, 36-INCH (0.914-M)-DEEP BED

Test No.	1	2	10	11	12	13	14	15	16
SO <sub>2</sub> Removal, %	67	91	70	70	82	91	91	91	88
NO <sub>x</sub> Removal, %	91	95	90	83	91	65	55	42	55
Inlet SO <sub>2</sub> (Dry), ppm by vol.	2350	2290	2950	2950	2950	2500	2500	2500	2400
Inlet NO <sub>x</sub> (Dry), ppm by vol.	550	530	460	460	460	590	590	590	465
Bed Temperature, °F	900	800	800	800	780	750	750	750	660
Sorbent Feed, lb/hr	340	998	1056	1056	1474	2982	2982	2982	2450
lb Sorbent/1000 scf	4.88	14.9	17.3	17.3	24.2	41.5	41.5	41.5	39.1
Available Cu, %	5.1	5.1	2.5	2.5	2.5	2.8	2.8	2.8	2.8
Cu/S Mole Ratio	0.65	2.00	0.89	0.89	1.27	2.76	2.76	2.76	2.70
Mole SO <sub>2</sub> Removed per Mole Available Cu	1.03	0.456	0.79	0.79	0.65	0.33	0.33	0.33	0.32
NH <sub>3</sub> /NO <sub>x</sub> Mole Ratio	1.1	0.97	0.95	0.83	0.92	0.46	0.36	0.28	0.45
Bed Inventory, lb (Measured after test)	1154	1034	1082	1082	1082	1114	1114	1114	1040
Pressure Drop, inches W.C.	24	24	23	24	24	24	24	24	23
Superficial Velocity, ft/s	4.0	3.6	3.3	3.3	3.2	3.7	3.7	3.7	3.0

TABLE 2. RESULTS OF FLUIDIZED-BED COPPER OXIDE PROCESS TESTS, 36-INCH (0.914-M)-DEEP BED, (CONTINUED)

Test No.	17	18	19	20	21	22	23	24	25
SO <sub>2</sub> Removal, %	88	88	89	89	89	89	89	90	90
NO <sub>x</sub> Removal, %	81	89	38	20	45	58	85	78	70
Inlet SO <sub>2</sub> (Dry), ppm by vol.	2400	2400	2250	2250	2250	2250	2250	2350	2350
Inlet NO <sub>x</sub> (Dry), ppm by vol.	465	465	970	800	800	800	800	970	970
Bed Temperature, °F	660	660	730	715	715	715	715	730	730
Sorbent Feed, lb/hr	2450	2450	2485	2485	2485	2485	2485	2596	2596
lb Sorbent/1000 scf	39.1	39.1	35.4	35.4	35.4	35.4	35.4	41.5	41.5
Available, Cu, %	2.8	2.8	2.9	2.9	2.9	2.9	2.9	3.1	3.1
Cu/S Mole Ratio	2.70	2.70	2.91	2.91	2.91	2.91	2.91	3.27	3.27
Mole SO <sub>2</sub> Removed per Mole Available Cu	0.32	0.32	0.31	0.31	0.31	0.31	0.31	0.28	0.28
NH <sub>3</sub> /NO <sub>x</sub> Mole Ratio	0.89	1.03	0.19	0	0.33	0.46	0.76	0.71	0.54
Bed Inventory, lb (Measured after test)	1040	1040	988	980	988	988	988	984	984
Pressure Drop, inches W.C.	23	23	23	23	23	23	23	23	23
Superficial Velocity, ft/s	3.0	3.0	3.1	3.1	3.1	3.1	3.1	3.1	3.1

°C = (°F-32)/1.8, kg/h = 2.205 lb/hr, m<sup>3</sup> = 35.31 ft<sup>3</sup>, Pa = 0.00402 inch W.C., kg = 2.205 lb, m/s = 3.281 ft/sec.

TABLE 3. RESULTS OF FLUIDIZED-BED COPPER OXIDE PROCESS TESTS, 18-INCH (0.457-M)-DEEP BED

Test No.	29	30	31	32	33	34	35	36	37
SO <sub>2</sub> Removal, %	70	70	70	78	78	78	84	84	84
NO <sub>x</sub> Removal, %	50	74	84	63	80	87	52	65	82
Inlet SO <sub>2</sub> (Dry), ppm by vol.	2340	2340	2340	2200	2200	2200	2150	2150	2150
Inlet NO <sub>x</sub> (Dry), ppm by vol.	500	500	500	520	520	520	620	620	620
Bed Temperature, °F	870	870	870	850	850	850	850	850	850
Sorbent Feed, lb/hr	1077	1077	1077	1850	1850	1850	1893	1893	1893
lb Sorbent/1000 scf	14.9	14.9	14.9	24	24	24	27.7	27.7	27.7
Available Cu, %	2.9	2.9	2.9	3.0	3.0	3.0	3.0	3.0	3.0
Cu/S Mole Ratio	1.11	1.11	1.11	1.96	1.96	1.96	2.30	2.30	2.30
Mole SO <sub>2</sub> Removed per Mole Available Cu	0.63	0.63	0.63	0.4	0.4	0.4	0.37	0.37	0.37
NH <sub>3</sub> /NO <sub>x</sub> Mole Ratio	0.46	0.75	0.93	0.51	0.73	0.87	0.37	0.6	0.89
Bed Inventory, lb (Measured after tests)	429	429	429	532	532	532	458	458	458
Pressure Drop, inches W.C.	16	16	16	16	17	17	17	17	17
Superficial Velocity, ft/s	4.1	4.1	4.1	4.3	4.3	4.3	3.8	3.8	3.8

°C = (°F-32)/1.8, kg/h = 2.205 lb/hr, m<sup>3</sup> = 35.31 ft<sup>3</sup>, Pa = 0.00402 inch W.C., kg = 2.205 lb, m/s = 3.281 ft/sec.

ature on performance of the 46-inch (1.17-m)-deep bed over the range of 750° to 860°F (399° to 460°C). However, data obtained with the 36-inch (0.914-m)-deep bed in the 660°-730°F (349°-388°C) range fall somewhat lower than the curve generated from data in the 750°-800°F (399°-427°C) range. The SO<sub>2</sub> removal efficiencies obtained in the 18-inch (0.457-m) bed are significantly lower than those obtained in the deeper beds, although the tests were conducted at fairly high temperatures (850°-870°F or 454°-466°C). There was no discernible effect of inlet SO<sub>2</sub> concentration on SO<sub>2</sub> removal efficiency in any of the tests.

#### NO<sub>x</sub> Removal

Results of NO<sub>x</sub> removal tests are given in Figures 5-7, which show NO<sub>x</sub> removal efficiency as a function of NH<sub>3</sub>/NO<sub>x</sub> mole ratio. At a given NH<sub>3</sub>/NO<sub>x</sub> mole ratio, the removal efficiencies in the 18-inch (0.457-m)-deep bed were only slightly lower than those obtained in the 36-inch (0.914-m)-deep bed; however, the 18-inch (0.457-m) bed tests were conducted at higher temperatures. Removal efficiencies obtained in the 46-inch (1.17-m) bed were higher than those obtained in the shallower beds over the

NH<sub>3</sub>/NO<sub>x</sub> range of ≈0.3-0.9. At a given bed depth, there was no discernible effect of either temperature or inlet NO<sub>x</sub> level on removal efficiency with the exception of data obtained in the 36-inch (0.914-m) bed (Figure 6) at 660°F (349°C), which indicate a slight decrease in NO<sub>x</sub> removal efficiency relative to data obtained in the 715°-800°F (379°-427°C) range.

#### Ammonia in Effluent Gas

An evaluation of NH<sub>3</sub> "slip" occurring in the reactor was conducted to determine whether NH<sub>3</sub> levels in the off-gas were acceptable. It is generally believed that NH<sub>3</sub> concentrations exceeding 30-40 ppm by volume could result in formation of ammonium salts that could plug or cause corrosion in downstream components.

Ammonia concentrations from 0 ppm to 12 ppm by volume were measured in the off-gas from the absorber during tests in which the NH<sub>3</sub>/NO<sub>x</sub> ratios in the flue gas were set from 0.5 to 1. The ammonia concentration was measured by passing a portion of the flue gas through a two-reactor NO/NO<sub>x</sub> analyzer. No evidence of ammonium salt formation was found in the piping downstream of the fluidized-bed reactor.

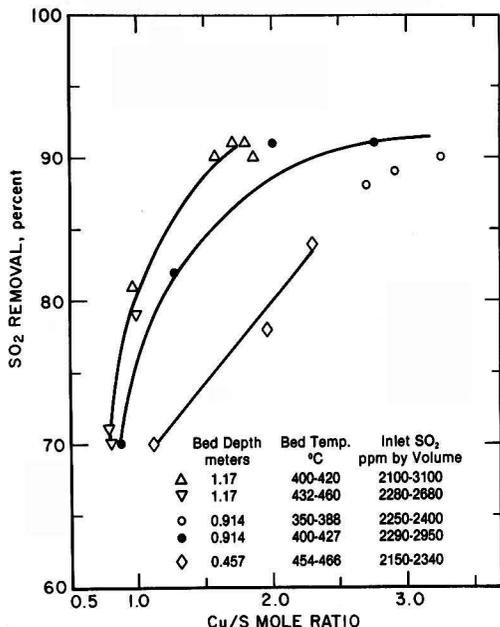


Figure 4. Effect of available-copper to inlet-sulfur ratio on SO<sub>2</sub>-removal efficiency.

#### Pressure Losses Through the Fluidized-Bed Reactor

Pressure drop across the distributor plate was typically about 10 inches W.C. (2488 Pa). Pressure drops through the sorbent bed were normally 6-7 inches W.C. (1493-1472 Pa) in the 18-inch (0.457-m)-deep bed; 13-14 inches W.C. (3235-3484 Pa) in the 36-inch (0.914-m)-deep bed; and 16-17 inches W.C. (3981-4230 Pa) in the 46-inch (1.17-m)-deep bed.

#### Sorbent Attrition

There has been no evidence of chemical attrition of the sorbent, i.e., loss of reactivity, in 24 sorption-regeneration cycles. However, physical attrition of the sorbent has been about 0.5% of the sorbent fed to the fluidized bed reactor, significantly higher than that observed in earlier PDU testing. The source of the attrition appears to be the rotary airlock feeder used in the test facility; batch tests con-

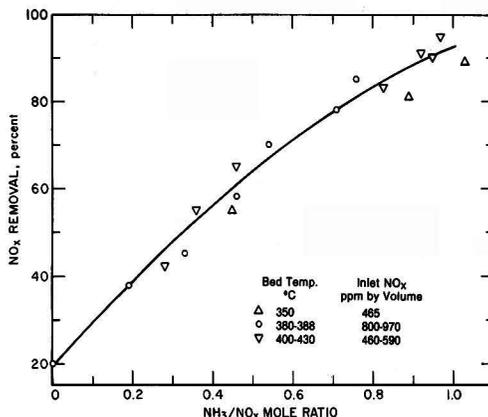


Figure 6. NO<sub>x</sub> removal in 36-inch (0.914-m)-deep bed.

ducted in the fluidized bed, with no sorbent feed or withdrawal, indicate attrition rates comparable to those found in earlier tests. Alternative sorbent feed systems are currently being evaluated. A slide-gate-valve and a V-pot ball-valve have been found to have substantially reduced the sorbent attrition.

#### CONCLUSIONS

Scale-up of the fluidized-bed reactor from the original 6-inch (15.2-cm)-diameter cylindrical configuration (used in PDU tests) to the 40-inch × 48-inch (0.1016-m × 0.219-m) rectangular configuration (a 60/1 scale-up) created no significant problems.

After 24 absorption/regeneration cycles, there was no indication of chemical attrition of the sorbent. Sulfur dioxide removal efficiencies in excess of 90% could readily be achieved throughout the test program.

Nitrogen oxides removal efficiencies in excess of 90% were achieved at NH<sub>3</sub>/NO<sub>x</sub> mole ratios of 1.0 or less. There was no evidence of ammonia "slip" in gases exiting the fluidized-bed reactor, nor was there evidence of ammonium salts deposition in ductwork downstream of the reactor.

There was no evidence of fly ash accumulation in the fluidized bed, nor was there any indication of ash deposition on the bed distributor plate.

Higher than expected physical attrition of the sorbent appears to be attributable to the rotary airlock feeder employed in the test facility.

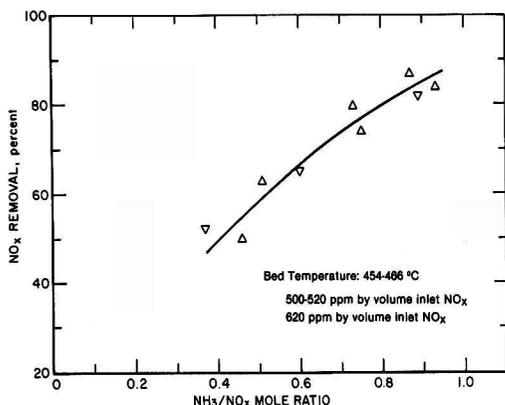


Figure 5. NO<sub>x</sub> removal in 18-inch (0.457-m)-deep bed.

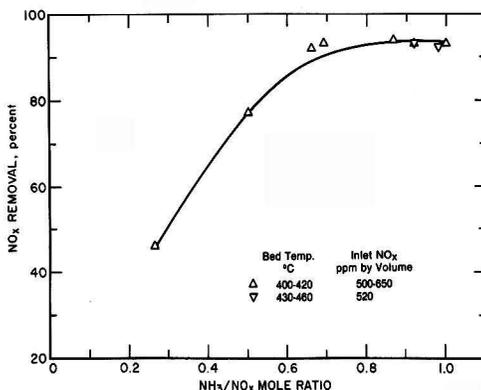


Figure 7. NO<sub>x</sub> removal in 46-inch (1.168-m)-bed.

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## LITERATURE CITED

1. McCrea, D. H., A. J. Forney, and J. G. Myers, "Recovery of Sulfur from Flue Gases Using a Copper Oxide Absorbent," *Journal of Air Pollution Control Association* **20**, No. 12 819-824 (Dec. 1970).
2. Strakey, J. P., E. R. Bauer, Jr., and W. P. Haynes, "Removal of SO<sub>2</sub> and NO<sub>x</sub> from Flue Gas in Fluidized-Bed Copper Oxide Process," Presented at the Sixth National Conference on Energy and the Environment, May 21-24, 1979, Pittsburgh, Pa. (Sponsored by APCA and AIChE).
3. Demski, R. J., S. J. Gasior, E. R. Bauer, Jr., J. T. Yeh, J. P. Strakey, and J. I. Joubert, "Simultaneous Removal of SO<sub>2</sub> and NO<sub>x</sub> from Flue Gas Employing a Fluidized-Bed Copper Oxide Process." Presented at the 1982 Summer National Meeting of the AIChE, August 29-September 1, 1982, Cleveland, Ohio.
4. Pohlentz, J. B. and A. O. Braun, "Treating Flue Gas from Coal-Fired Boilers for NO<sub>x</sub> Reduction with the Shell Flue Gas Treating Process," EPA/EPRI Joint Symposium on Stationary Combustion NO<sub>x</sub> Control, Denver, Colo., October 6-9, 1980.
5. Jones, G. D. and J. D. Mobley, "Selective Catalytic Reduction and NO<sub>x</sub> Control in Japan," A Status Report by the Radian Corp., DCN 81-203-001-27-07, Jan. 1981.
6. Burke, J. M., "Independent Evaluation of the Shell Flue Gas Treatment Process" (A Radian Corporation Report to the Environmental Protection Agency, EPA Contract No. 68-02-3171).



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# Oxidation of 2-Chlorophenol Using Ozone and Ultraviolet Radiation

This type of reaction system has great potential for the destruction of refractory organic water pollutants in industrial effluents.

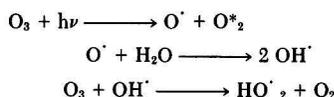
Shahab R. Khan, Ching R. Huang, Joseph W. Bozzelli, New Jersey Institute of Technology, Newark, N.J. 07102

2-Chlorophenol has been on the US EPA's priority pollutants list since 1978 [1]. Its concentration in drinking water has been limited to 0.3  $\mu\text{g/liter}$  [2]. The degradation of 2-chlorophenol by biological oxidation has been found to be ineffective at concentrations higher than 40 ppm [3].

Ozone has been found to be an effective oxidizing agent for the removal of many organic pollutants from water. It is often preferred over chlorination because it has a higher oxidation potential than chlorine (see Table 1). Unlike chlorine, ozonation does not result in the formation of stable acids as a last step and, recently, chlorination has been linked to the production of trihalomethanes such as chloroform, methylene chloride, and carbon tetrachloride [4, 5].

Ozonation in the presence of ultraviolet light has been found to be a more effective technique than ozonation alone. Prengle and co-workers, in a series of experiments, determined that ozone/UV oxidation is extremely effective in the destruction of toxic pollutants in water, where the UV radiation is believed to be responsible, in many cases, for activating the toxic compound and/or decomposing the dissolved ozone itself. As a result, oxidation rates with ozone/UV are 10 to 1000 times faster than ozone alone [6-10].

Both the mechanism and kinetics of the decomposition of ozone in water are somewhat uncertain. Prengle and Mauk presented a reaction scheme for generation of active species from ozone in the presence of UV radiation. A brief and simplified initiation scheme suggested by Prengle is given below [14, 16].



where  $\{\text{M}^\cdot\}$  is a free radical species which will rapidly undergo further reaction.

The overall mechanism is  $\text{O}_3/\text{UV}$  photo-oxidation of chemical species in aqueous solutions occurs by a combination of reactions with the following:

- O and  $\text{O}^{\cdot 2}$  species resulting from the photolysis of ozone.
- $\text{OH}^\cdot$  and  $\text{HO}^\cdot_2$  species resulting from the photolysis and subsequent reactions of ozone with water and organics present in water.
- Photolysis of the chemical species "M" itself to produce  $\text{M}^*$  and free radicals.

These species participate in a series of oxidation reactions leading to the final oxidation products, which, for hydrocarbons, are ultimately  $\text{CO}_2$  and water. Table 1 shows the comparison of these species with several other oxidations.

This paper presents experimental data and proposed kinetic schemes for the oxidation of 2-chlorophenol with ozone, with ultraviolet light, and with ozone/UV combined. The objective is to develop a mechanistic expression for the ozone/UV process, from which, knowing the given ozone dose rate and UV intensity, the disappearance curve for substrate may be predicted; i.e., its degradation may be modelled and optimized for the application.

Our work differs from that of Prengle's in that the latter has defined a refractory index which is a measure of difficulty to oxidize compounds by ozone alone [9, 10]. In this study, specific kinetic rates are determined based upon experimental results from a series of reactions on 2-chlorophenol using an optimization program on a computer.

## EXPERIMENTAL

### Reactor

A schematic diagram of the apparatus used for mass transfer and kinetic observations is shown in Figure 1. The reactor has a liquid holdup volume of 40 liters. It is a semi-batch type which also has the capability to operate as a continuous flow stirred tank reactor (CFSTR). It is a vertical cylinder with nine sample ports along the cylindrical axis (six inches apart). The dimensions of the reactor are such as

TABLE 1. COMPARISON, OXIDATION POTENTIAL OF OZONE AND ITS PHOTOLYSIS SPECIES.

Species	Oxidation Potential (volts)	Relative Oxidation power*
Fluorine, $\text{F}_2$	3.06	2.25
Hydroxyl Radical, $\text{OH}^\cdot$	2.80	2.05
Atomic Oxygen, O	2.42	1.78
Ozone, $\text{O}_3$	2.07	1.52
Hydrogen Peroxide, $\text{H}_2\text{O}_2$	1.77	1.30
Perhydroxyl Radical, $\text{HO}_2^\cdot$	1.70	1.25
Hypochlorous Acid, $\text{HOCl}$	1.49	1.10
Chlorine, $\text{Cl}_2$	1.36	1.00

\*Based on  $\text{Cl}_2$  as a reference.

to facilitate scale up in view of the correlations outlined by Prengle and Barona [11]. Ozone gas is introduced into the reactor from the bottom through stainless steel spargers of medium (2-micron) porosity. Ozone exits from the top of the reactor to an exhaust hood via a vent line. The reactor is made of clear acrylic plastic and can be dismantled easily for cleaning after each kinetic run. There are no mechanical agitators used in the reactor. Complete mixing is achieved by bubbling the gas up through the reactor. Tracer runs with sodium hydroxide showed that a uniform pH is achieved in approximately 1.50 minutes at the gas ( $O_2/O_3$ ) flows used in kinetic runs.

Ozone is produced using an ozone generator (model T-816 Welsbach Systems Corporation, Philadelphia, Pa.). It is a water cooled, corona discharge type. Ozone output is adjustable by varying power input to the discharge using a Variac on the generator.

The ultraviolet light source was obtained from Conrad-Hanovia Inc., Newark, NJ. It is an immersion type, high pressure mercury vapor lamp with an arc length of 25 inches and has a power rating of 5 kW. The lamp is encased in two concentric wells made of quartz. These immersion wells provide a cooling jacket around the lamp and keep any explosive vapors, which may form, away from the lamp. Figure 2 shows the wave length spectrum and intensities obtained from this lamp as supplied by the manufacturer.

#### Ozone Mass Transfer From Gas to Liquid Phase

To study the rate of ozone absorption in water, the reactor was filled with distilled water, a desired temperature was maintained, and the ozonator was then started. Ozone

gas initially produced was bled from the ozonator to the vent hood for the first few minutes to purge the generator, and was then switched into the reactor. Water samples were withdrawn from a sample port at fixed time intervals to determine the ozone solubility equilibrium at different temperatures. The concentrations *versus* time data leading to the calculation of mass transfer coefficients is shown in Figure 3.

To determine the ozone concentration gradient in the reactor, samples were withdrawn from sample ports at various heights from the disperser, all at a fixed time. Equilibrium was reached within 10 minutes, as shown in Figure 4.

#### Ozone Decomposition with Ultraviolet Light

Ozone decomposition with UV light was also determined in a similar experimental manner. Once dissolved ozone reached equilibrium, the UV lamp was turned on and, after a warm up period of about 30 seconds, water samples were withdrawn at regular time intervals. This experiment required extra precaution in order to avoid errors due to the relatively fast ozone decomposition reaction, so the sample collection and analysis time was kept short. Samples collected from these experiments were subjected to analysis within 7-8 minutes.

When UV light was turned on, no ozone was detected in water samples withdrawn from sample ports directly in front of the UV lamp. A small quantity of ozone was, however, detected in samples withdrawn from the sample port 12 inches below the lamp as shown in Figure 10.

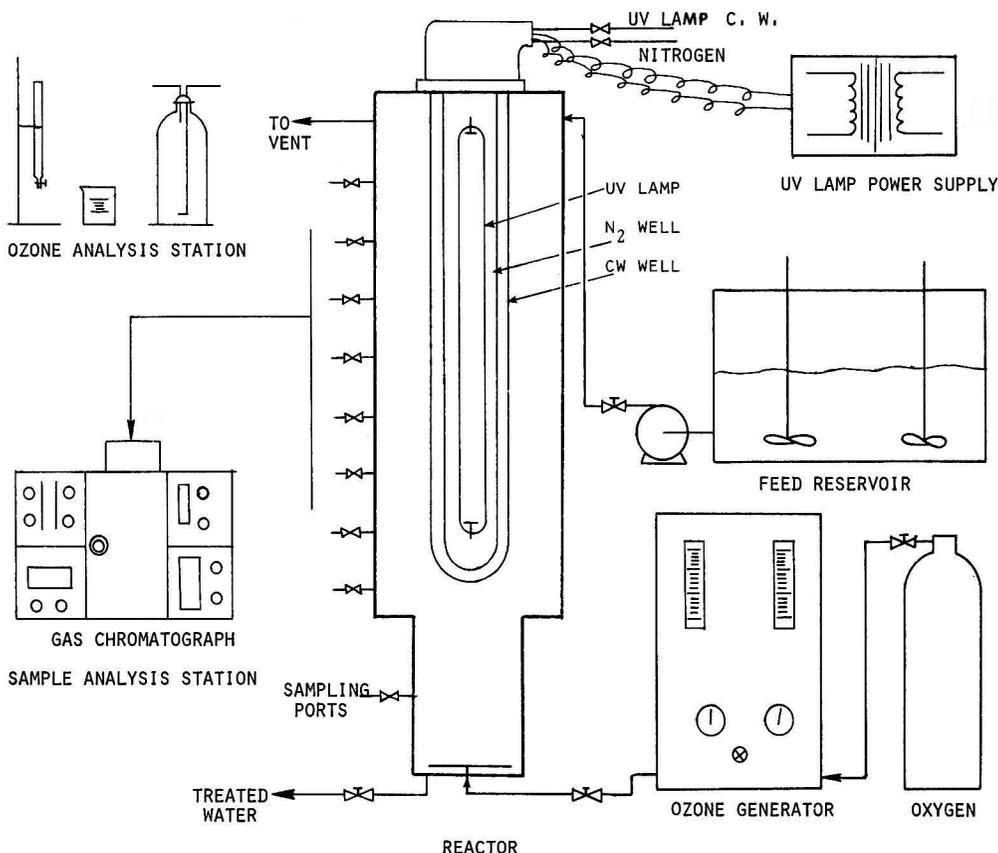


Figure 1. Schematic diagram of apparatus used for kinetic and mass transfer experiments.

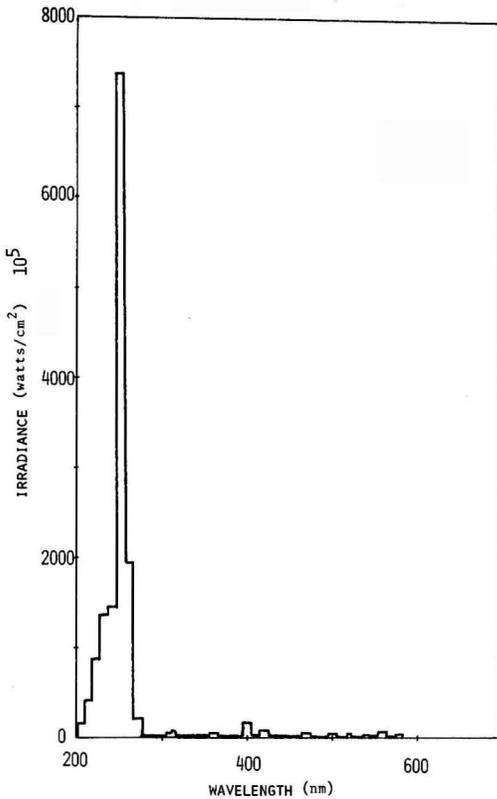


Figure 2. Spectral distribution from ultraviolet lamp in 200-600 nm region.

### Decomposition of 2-Chlorophenol

Feed liquor was prepared by dissolving the desired amount of 2-chlorophenol in 40 liters of distilled water. It was then transferred to the reactor. The first few liters of feed were purged from the reactor for the purpose of conditioning the system. Nitrogen gas was bubbled through the reactor for several minutes to detect any possible vapor stripping effect. The initial concentration of 2-chlorophenol in water was kept around 200 ppm. Each experiment was repeated at least twice to determine the reproducibility of the results.

### ANALYTICAL PROCEDURES

The concentration of ozone in water samples was determined immediately after withdrawal of the samples. The iodometric method, as described in Reference [13] was followed for the determination of ozone in water as well as in the inlet and outlet gas streams.

The concentration of 2-chlorophenol was determined by using a gas chromatograph equipped with a flame ionization detector. The column used was glass (for inertness), six feet long, 1/8 in. I. D., packed with 3% SP-2100 on 100/120 Supelcoport. 0.5  $\mu$ l of sample was injected directly at the column. The oven temperature was maintained at 70°C for 2 minutes, increasing it to 130°C at a rate of 32°C/min. Each sample was analyzed at least twice, or until similar peak areas were obtained.

### RESULTS AND DISCUSSION

The experimental results and rate constants computed from them are discussed below. Details of mass transfer and kinetic models are given in the Appendix.

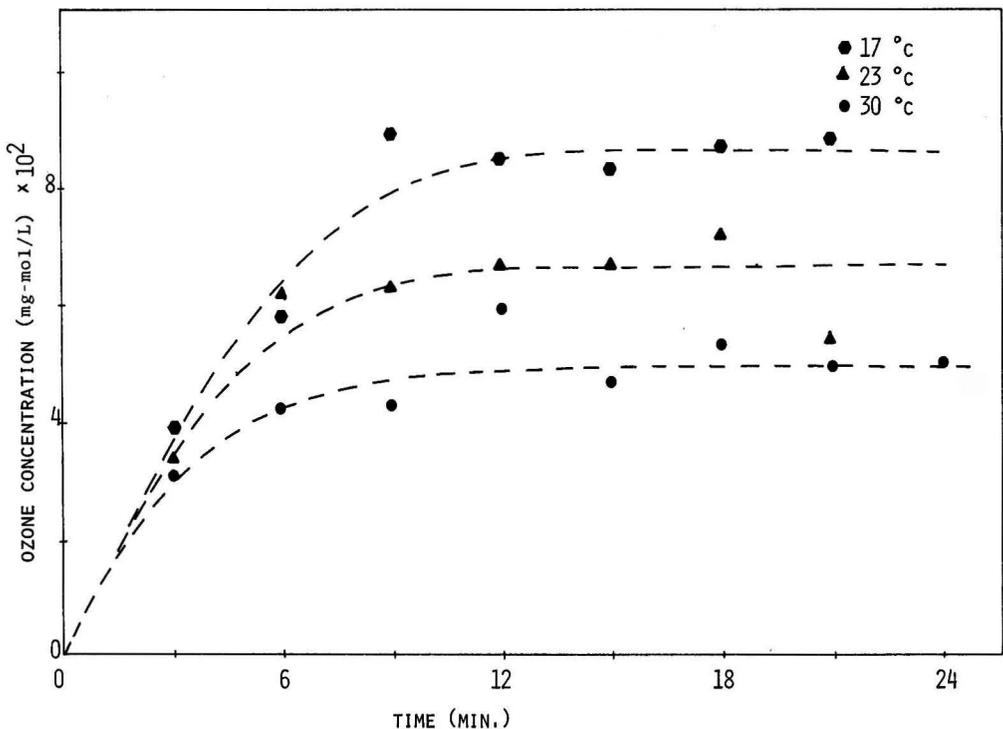


Figure 3. Ozone solubility in water at different temperatures. at 17°C at 23°C at 30°C

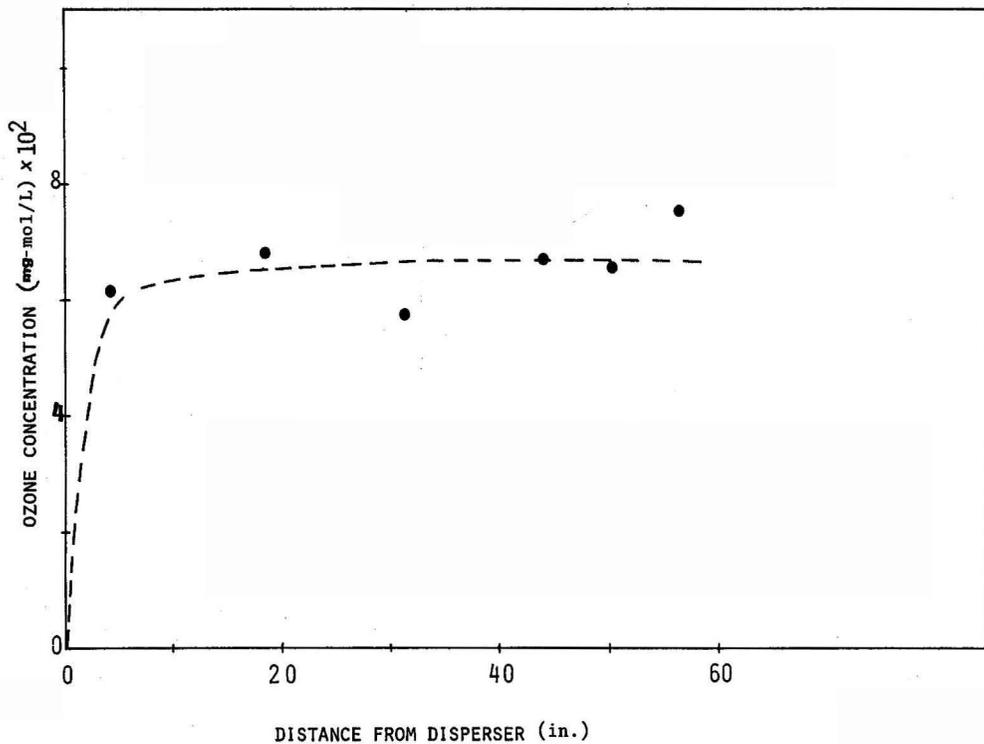


Figure 4. Ozone concentration gradient in the reactor.  
 Sampling time = 10 minutes  
 Temperature = 23°C

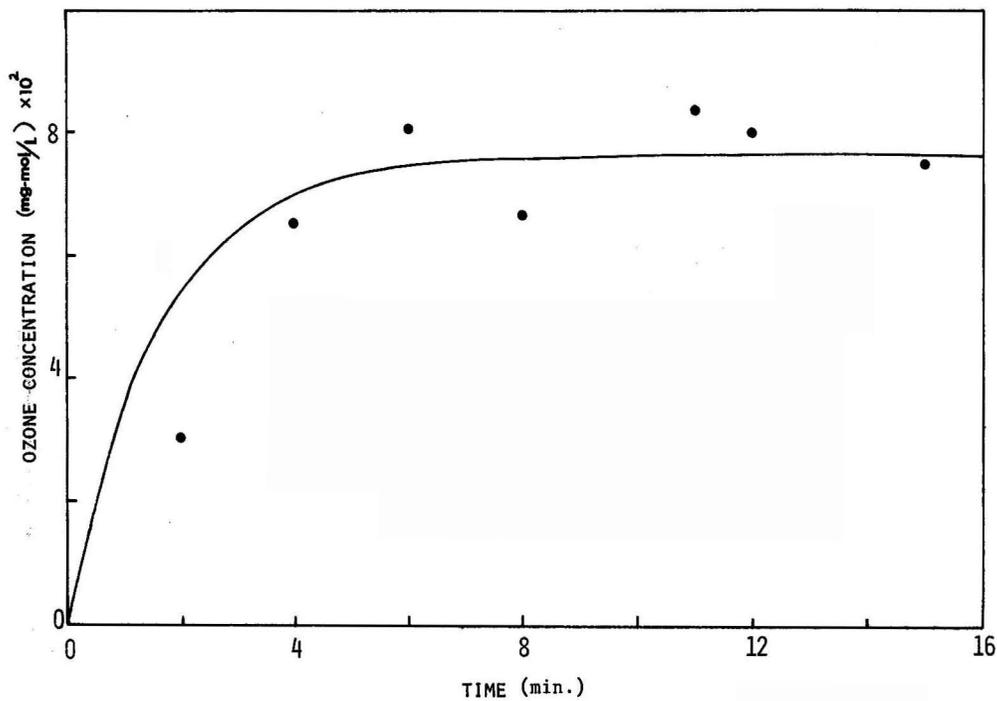


Figure 5. Ozone equilibrium in water at 23°C.

### Mass Transfer of Ozone From Gas to Liquid Phase

The solubility of ozone in water is greatly dependent upon temperature, as shown in Figure 3. All the experiments were carried out at an initial pH range of 6.5 to 7.5. Equation (1.1), resulting from a mass balance of ozone over the liquid phase, was solved with the help of experimental data. In this equation, the concentration of ozone at the interphase ( $CO_{3i}$ ) is assumed constant and equal to the concentration in the gas stream. The ozone concentration in the liquid phase ( $CO_{3L}$ ) is available as a function of time from experimental data. The value of the mass transfer coefficient  $K_{LO_3}a$  is found by linear regression using a computer program. The value of the mass transfer coefficient (combined with the interfacial surface area "a"), which gave the best fit to the experimental data is  $0.6363 \text{ (min)}^{-1}$ . Figure 5 shows a comparison of this coefficient with experimental results.

### Oxygen Mass Transfer from Gas to Liquid Phase

The ozone was fed into the reactor as a mixture of ozone and oxygen gases. Since oxygen itself is activated with UV light, its solubility in water was determined by passing a stream of pure oxygen into the reactor. Oxygen reaches its equilibrium value very rapidly and its solubility in water is less temperature-dependent than ozone. Equation (2.1), resulting from an oxygen mass balance over the liquid phase, is solved with the help of experimental data by using a similar algorithm to the case of ozone mass transfer. The value of the oxygen mass transfer coefficient, combined with the interfacial surface area, which gave the best fit to the experimental data is  $K_{LO_2}a = 1.62 \text{ (min)}^{-1}$ . The fit

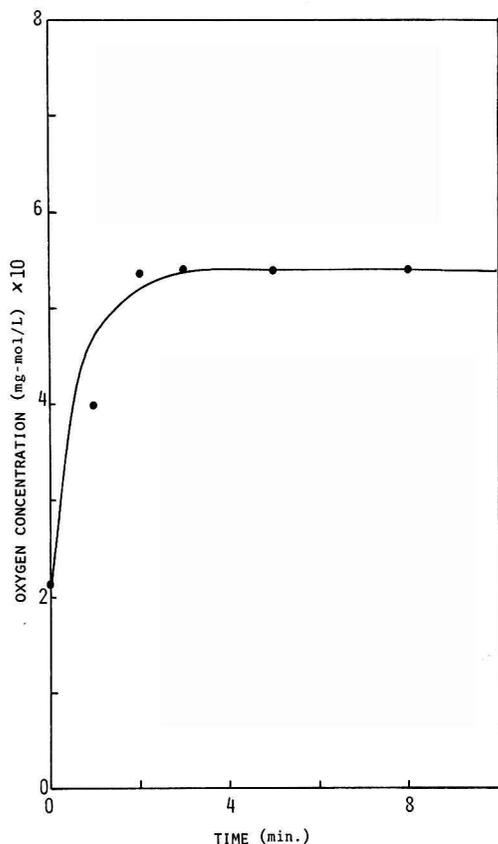


Figure 6. Oxygen equilibrium in water at 26°C.

of the calculated curve versus the experimental data points is shown in Figure 6. The final oxygen concentration in water, determined at 26°C, is  $0.54 \text{ mg-mol/liter}$  or about 17 ppm.

### Oxidation of 2-Chlorophenol with Ozone

The oxidation of 2-chlorophenol with ozone alone was carried out at operating conditions and ozone flow rate identical to those of mass transfer experiments. The two differential equations resulting from mass balance of ozone and 2-chlorophenol (Equations 3.1 and 3.2 in Appendix) were solved by a Runge-Kutta fourth-order numerical method on a computer. The optimized value of the reaction rate constant  $k_1$  was calculated by using Rosenbrock's "Hill-Climb" optimization program [15].

The optimum value of  $k_1$  is  $2.273 \text{ (mg-mol/liter)}^{-1} \text{ (min)}^{-1}$ . A comparison of this rate is constant to the experimental data is shown in Figure 7.

### Decomposition of 2-Chlorophenol with UV Light Alone

The UV oxidation of 2-chlorophenol was carried out by pouring nitrogen gas instead of ozone into the reactor to bring about the same mixing effect as in the case of the ozone/ $O_2$ . Decomposition of 2-chlorophenol with UV light was a relatively slow reaction. Only about 62% conversions was achieved in 4 hours. Equations (4.1) and (4.2) were solved numerically by the RK-4 method used above. Three reaction rate constants,  $K_{IA1}$ ,  $k_2$ , and  $k_3$  were optimized by Rosenbrock's "Hill-Climb" optimization program on the computer.

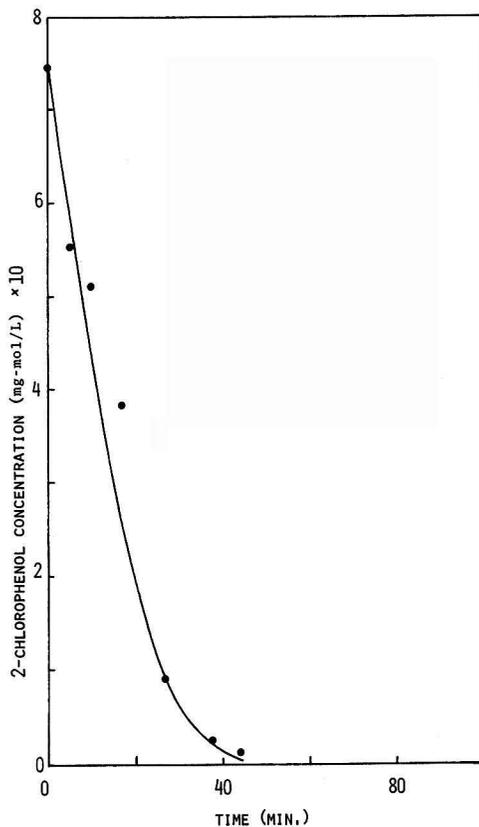


Figure 7. Oxidation of 2-chlorophenol with ozone.

The values of the rate constants which gave the best fit to the experimental data are:

$$\begin{aligned}k_{1A}I &= 0.013 \text{ (min)}^{-1} \\k_2 &= 0.0071 \text{ (min)}^{-1} \\k_3 &= 0.013 \text{ (min)}^{-1}\end{aligned}$$

The theoretical curve based upon these values and its fit to the experimental data is shown in Figure 8.

#### Decomposition of 2-Chlorophenol with Oxygen and UV Light

The theoretical curve resulting from solving equation set (5.1) is shown in Figure 9. The optimized values of rate constants used in this curve are given below;

$$\begin{aligned}k_{1O_2}I &= 0.24 \text{ (min)}^{-1} \\k_5 &= 0.26 \text{ (mg-mol/liter)}^{-1} \text{ (min)}^{-1} \\k_6 &= 0.86 \text{ (min)}^{-1}\end{aligned}$$

#### Decomposition of 2-Chlorophenol with Ozone/UV

The decomposition of 2-chlorophenol with ozone in the presence of ultraviolet radiation is a faster reaction than any of the conversion reactions discussed above. The experimental results of this reaction are shown in Figure 11. A comparison with oxygen/UV reaction (Figure 9) shows that the ozone/UV reaction is about 45% faster than oxygen/UV, indicating that ozone is important for the rapid oxidation of 2-chlorophenol. A comparison of Figure 11 with Figure 8 shows that UV oxidation of 2-chlorophenol

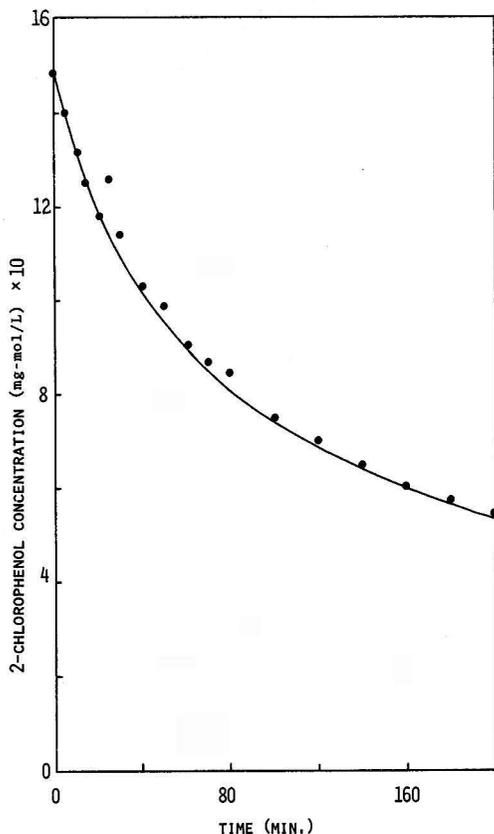


Figure 8. Decomposition of 2-chlorophenol with UV light.

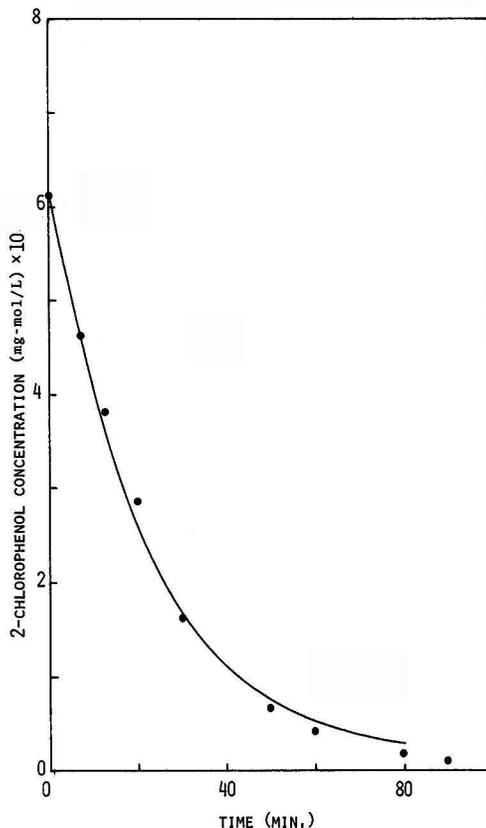


Figure 9. Oxidation of 2-chlorophenol with O<sub>2</sub> and UV light.

without ozone was even slower, indicating that ultraviolet light is not as effective as ozone/UV.

A mechanism for the ozone/UV reaction with the specific organic pollutant, 2-chlorophenol, is proposed and shown in the Appendix. This reaction scheme is being subjected to further investigation and improvements as a part of continuing research on this project. It is noted that the production and reaction of the free radical species OH<sup>·</sup> (hydroxyl) is omitted in this reaction mechanism, as cited by Prengle [16] and Hoigne' [17]. This is done because the inclusion of additional unknown rate constants into our experimental parameter set would yield too many variables for significant computational modeling. We are presently trying to determine specific rate parameters for OH<sup>·</sup> reactions and production in aqueous solutions from the literature for inclusion so that we may extend the set of rate equations to a more accurate set.

The six differential equations (6.1 to 6.6 in Appendix) resulting from a material balance on this reaction scheme were solved by the Runge-Kutta fourth order numerical method using the data from each of the above-mentioned experimental studies. The optimized values of the reaction rate constants which gave the best fit to the experimental data are;

$$\begin{aligned}k_{1O_3}I &= 0.8 \text{ (min)}^{-1} \\k_4 &= 4.1 * 10^{-6} \text{ (mg-mol/liter)}^{-1} \text{ (min)}^{-1} \\k_7 &= 2.381 * 10^{-3} \text{ (mg-mol/liter)}^{-1} \text{ (min)}^{-1}\end{aligned}$$

Figure 11 shows the destruction curve of 2-chlorophenol vs. time, based upon these rate constants and the model's fit to the experimental data.

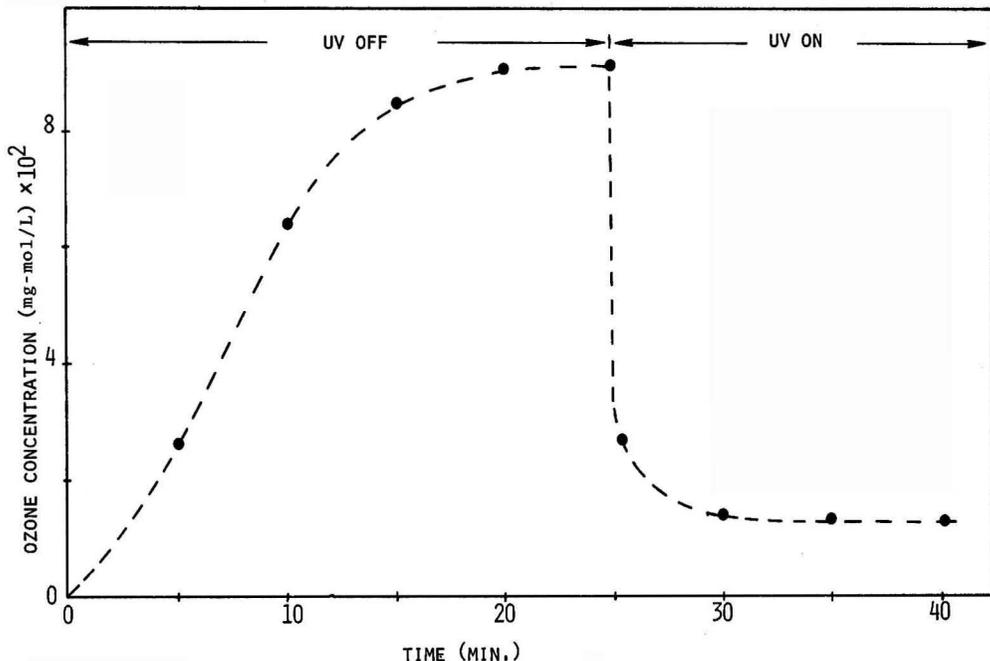


Figure 10. Ozone decomposition with UV light (at 15°).

#### APPENDIX:

#### MATHEMATICAL MODELS FOR MASS TRANSFER AND REACTION KINETICS IN A SEMI-BATCH REACTOR

Six models are developed to justify the experimental data. 1) Ozone mass transfer, 2) oxygen mass transfer, 3) reaction of 2-chlorophenol with ozone, 4) decomposition of 2-chlorophenol with UV light, 5) reaction with oxygen and UV light, and 6) reaction of 2-chlorophenol with ozone/UV.

##### 1. Mass Transfer of Ozone from Gas to Liquid Phase

A mass balance of ozone over the liquid phase gives;

$$K_{L_{O_3}} a V (C_{O_3g} - C_{O_3l}) = V \frac{dC_{O_3l}}{dt}$$

Since  $C_{O_3g}$  is constant,  $-dC_{O_3l}$  may be written as  $d(C_{O_3g} - C_{O_3l})$ . Multiplying the above equation by  $-1$  and integrating, boundary conditions are

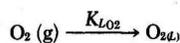
$$\text{at } t = 0 \quad C_{O_3l} = 0$$

$$t = t \quad C_{O_3l} = C_{O_3l}$$

$$\frac{C_{O_3g} - C_{O_3l}}{C_{O_3g}} = e^{-k_{L_{O_3}} a t} \quad (1.1)$$

This equation is solved by linear regression of experimental data of  $C_{O_3l}$  vs  $t$ .

##### 2. Mass Transfer of Oxygen from Gas to Liquid Phase



The oxygen mass balance over the liquid volume yields,

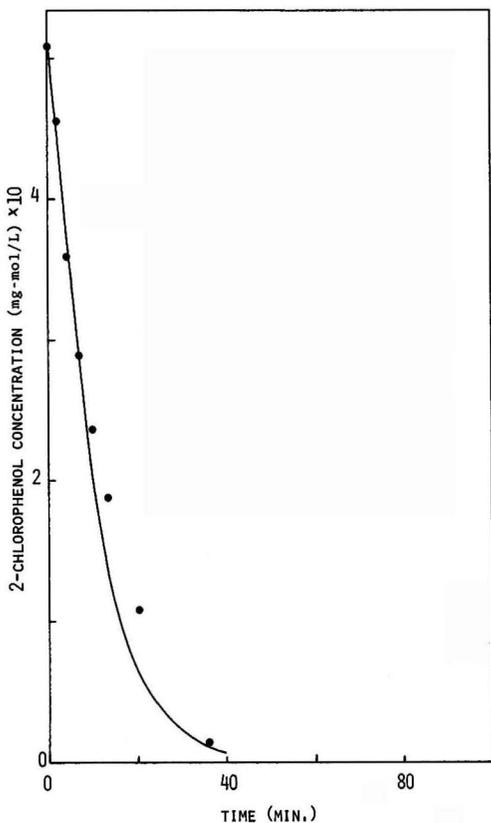


Figure 11. 2-chlorophenol oxidation with ozone and UV light.

$$\frac{dC_{O_2}}{dt} = K_{L_{O_2}} a (C_{O_2}^* - C_{O_2})$$

solving this differential equation with the help of following boundary conditions,

$$\text{at } t = 0 \quad C_{O_2} = C_{O_2 t=0}$$

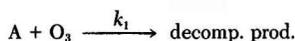
gives

$$C_{O_2} = C_{O_2}^* \left[ 1 - \left( \frac{C_{O_2}^* - C_{O_2 t=0}}{C_{O_2}^*} \right) e^{-K_{L_{O_2}} a t} \right] \quad (2.1)$$

### 3. Reaction of 2-Chlorophenol with Ozone

The reaction is represented by the following stoichiometric equation,

$$\frac{\bar{C}_A}{C_{A(0)}} = \frac{S + \frac{k_2 + k_3 + k_{1A}I}{2} + \frac{k_2 + k_3 - k_{1A}I}{2}}{\left( S + \frac{k_2 + k_3 + k_{1A}I}{2} \right)^2 - \left[ \frac{(k_2 + k_3 + k_{1A}I)^2}{2} - k_2 k_{1A}I \right]} \quad (4.6)$$



the rate equation is,

$$v_A = \frac{dC_A}{dt} = -k_1 C_A C_{O_3} \quad (3.1)$$

material balance of ozone gives

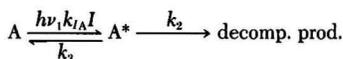
$$\frac{dC_{O_3}}{dt} = k_{1_{O_3}} \alpha (C_{O_3}^* - C_{O_3}) - k_1 C_A C_{O_3} \quad (3.2)$$

Equations (3.1) and (3.2) are solved simultaneously by the Runge-Kutta 4th order method. The resulting equation is solved for  $k_1$  with the help of experimental data. The value of  $k_1$  was then optimized using an optimization program [15] to find that value of  $k_1$  which gives minimum deviation from the experimental data.

### 4. Decomposition of 2-Chlorophenol with UV Light

The reaction is represented by the following equation,

$$\frac{C_A}{C_{A(0)}} = e^{-\frac{k_2 + k_3 + k_{1A}I}{2} t} \cosh \sqrt{\frac{(k_2 + k_3 + k_{1A}I)^2}{4} - k_2 k_{1A}I} t + \frac{\frac{k_2 + k_3 - k_{1A}I}{2}}{\sqrt{\frac{(k_2 + k_3 + k_{1A}I)^2}{4} - k_2 k_{1A}I}} e^{-\frac{k_2 + k_3 + k_{1A}I}{2} t}$$



Material balance of reactant A (2-chlorophenol) over the reactor volume gives,

$$\frac{dC_A}{dt} = -k_{1A}I C_A + k_3 C_{A^*} \quad (4.1)$$

material balance of intermediate  $A^*$  gives,

$$\frac{dC_{A^*}}{dt} = k_{1A}I C_A - k_2 C_{A^*} - k_3 C_{A^*} \quad (4.2)$$

taking Laplace transforms of Eq. (4.1) and (4.2)

$$S \bar{C}_A = -C_{A(0)} = -k_{1A}I \bar{C}_A + k_3 \bar{C}_{A^*} \quad (4.3)$$

$$S \bar{C}_{A^*} = k_{1A}I \bar{C}_A - k_2 \bar{C}_{A^*} - k_3 \bar{C}_{A^*} \quad (4.4)$$

since  $C_{A^*}$  is not known, from Eq. (4.4),

$$\bar{C}_{A^*} = \frac{k_{1A}I}{S + k_2 + k_3} \bar{C}_A \quad (4.5)$$

substituting it into Eq. (4.3) and rearranging,

Let,

$$a = \left[ \frac{(k_2 + k_3 + k_{1A}I)^2}{4} - k_2 k_{1A}I \right]^{1/2}$$

$$b = -\frac{k_2 + k_3 + k_{1A}I}{2}$$

$$c = \frac{k_2 + k_3 + k_{1A}I}{(S - a)^2 - a^2}$$

$$\frac{\bar{C}_A}{C_{A(0)}} = \frac{S - b + c}{(S - b)^2 - a^2} \quad (4.7)$$

taking the inverse Laplace transform of Eq. (4.7),

$$\frac{C_A}{C_{A(0)}} = e^{bt} \cosh at + \frac{c}{a} e^{bt} \sinh at$$

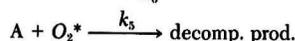
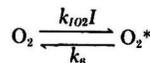
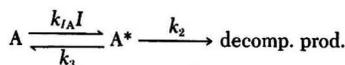
substituting the values of  $a$ ,  $b$ , and  $c$ ,

$$\text{Sinh} \sqrt{\frac{(k_2 + k_3 + k_{1A}I)^2}{4} - k_2 k_{1A}I} t \quad (4.8)$$

this equation is solved with experimental data to find the optimized values of the rate constants.

### 5. Reaction with Oxygen and UV Light

The reaction scheme is,



Material balances for each component yield,

$$\frac{dC_A}{dt} = -k_5 C_A C_{O_2^*} - k_{1A} I C_A + k_3 C_{A^*}$$

$$\frac{dC_{A^*}}{dt} = k_{1A} I C_A - k_2 C_{A^*} - k_3 C_{A^*}$$

$$\frac{dC_{O_2}}{dt} = k_{L_{O_2}} a (C_{O_2l} - C_{O_2}) - k_{1_{O_2}} I C_{O_2} + k_6 C_{O_2^*}$$

$$\frac{dC_{O_2^*}}{dt} = k_{1_{O_2}} I C_{O_2} - k_5 C_A C_{O_2^*} - k_6 C_{O_2^*}$$

initial conditions,

$$C_A = C_{A0}$$

$$C_{O_2} = C_{O_2 t=0}$$

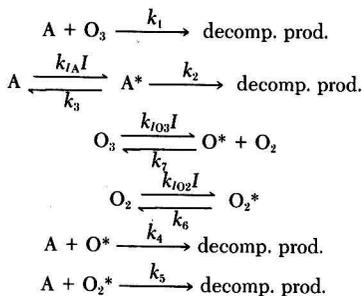
$$C_{O_2^*} = 0$$

$$C_{A^*} = 0$$

the simultaneous differential equations (5.1) are solved by the 4th-order Runge-Kutte method. The values of the rate constants  $k_{1_{O_2}} I$ ,  $k_5$ , and  $k_6$  are optimized to give the best fit to the experimental data.

#### 6. Ozone/UV Reaction of 2-Chlorophenol

The reaction scheme for this reaction system is given as,



mass balance of each component,

$$\frac{dC_A}{dt} = -k_1 C_A C_{O_3} - K_{1A} I C_A + K_3 C_{A^*} - k_4 C_A C_{O^*} - k_5 C_A C_{O_2^*} \quad (6.1)$$

$$\frac{dC_{A^*}}{dt} = k_{1A} I C_A - k_3 C_{A^*} - k_2 C_{A^*} \quad (6.2)$$

$$\frac{dC_{O_3}}{dt} = -k_1 C_A C_{O_3} - k_{1_{O_3}} I C_{O_3} + k_7 C_{O^*} C_{O_2} + K_{L_{O_3}} a (C_{O_3l} - C_{O_3}) \quad (6.3)$$

$$\frac{dC_{O^*}}{dt} = k_{1_{O_3}} I C_{O_3} - k_7 C_{O^*} C_{O_2} - k_4 C_A C_{O^*} \quad (6.4)$$

$$\frac{dC_{O_2}}{dt} = -k_{1_{O_2}} I C_{O_2} + k_{1_{O_3}} I C_{O_3} - k_7 C_{O^*} C_{O_2} + k_6 C_{O_2^*} + K_{L_{O_2}} a (C_{O_2l} - C_{O_2}) \quad (6.5)$$

$$\frac{dC_{O_2^*}}{dt} = k_{1_{O_2}} I C_{O_2} - k_6 C_{O_2^*} - k_5 C_A C_{O_2^*} \quad (6.6)$$

these differential equations are solved with the following initial conditions,

$$C_A = C_{A0}$$

$$C_{A^*} = 0$$

$$C_{O_3} = 0$$

$$C_{O^*} = 0$$

$$C_{O_2} = C_{O_2 t=0}$$

$$C_{O_2^*} = 0$$

The resulting six equations are solved with the help of three sets of experimental data, namely, A-O<sub>3</sub> vs. time, A-UV vs. time, and A-O<sub>2</sub> vs. time. The values of the three unknown rate constants,  $k_{1_{O_3}} I$ ,  $k_7$  and  $k_4$  thus obtained are then optimized to give the best fit to the experimental results of this experiment.

#### CONCLUSIONS

Destruction of 2-chlorophenol in water at several hundred concentrations by reaction with ozone and ultraviolet light has been shown to be significantly faster than reaction with either ozone or UV radiation alone. Complete reaction, to less than 1 ppm, is accomplished within 50 minutes using lab scale ozone and UV generation equipment in a pilot scale reactor.

A mechanism was proposed and detailed rate constants were obtained, in addition to mass transfer coefficients, permitting accurate calculation (modeling) of the global reaction scheme. It is also shown that this type of reaction system has a high degree of potential for destruction of refractory organic water pollutants in industrial effluent.

#### NOMENCLATURE

A designates 2-chlorophenol

a = Effective interfacial area of gas per unit volume of liquid or reactor [cm<sup>2</sup>/cm<sup>3</sup> of reactor]

I = Intensity of UV radiation [W/cm<sup>2</sup>]

M = Chemical species (pollutant)

t = time [min]

$k_L$  = Mass transfer coefficient for liquid phase [cm/min]

$k_I$  = Reaction rate constant for reactions in the presence of UV light [(min)<sup>-1</sup>].

$k_1$  = Chemical reaction rate constant for ozone -2-chlorophenol reaction [(mg-mol/liter)<sup>-1</sup>]

$k_2$  = Chemical reaction rate constant for the decomposition of 2-chlorophenol with UV light [(min)<sup>-1</sup>]

$k_3$  = Reaction rate constant for the reverse reaction of 2-chlorophenol with UV light [(min)<sup>-1</sup>]

$k_4$  = Reaction rate constant for ozone-UV oxidation of 2-chlorophenol [(mg-mol/liter)<sup>-1</sup> (min)<sup>-1</sup>]

$k_5$  = Reaction rate constant for oxygen-UV reaction of 2-chlorophenol [(mg-mol/liter)<sup>-1</sup> (min)<sup>-1</sup>]

$k_6$  = Reaction rate constant for oxygen decomposition with UV light [(min)<sup>-1</sup>]

$K_7$  = Reaction rate constant for reversible decomposition of ozone with UV light [(mg-mol/liter)<sup>-1</sup> (min)<sup>-1</sup>]

O<sub>3</sub> = Ozone

O<sub>2</sub> = Oxygen

#### Subscripts

I = Interphase

L = Liquid phase

#### Superscript

\* = Reactive species in excited state.

## LITERATURE CITED

1. Keith, L. H., Water—1980 *AICHE Symp. Ser.*, **77**, (209), 249 (1981).
2. *Federal Register* **44**, (52) 15946 (Mar. 15, 1979).
3. Private communications with Dr. G. Lewendowski, Dept. of Chemical Eng. New Jersey Institute of Technology, Newark, N.J. (1984).
4. Rook, J. J., *Water Treatment and Examination*, **23**, (2), 234 (1974).
5. Beller, T. A., J. J. Lichtenberg, and R. C. Kroner, *Journal of Water Works Association*, **66**, 703 (1974).
6. Prengle, H. W. *et al.*, Hydrocarbon Processing (October 1975).
7. Prengle, H. W., C. E. Mauk, and J. E. Payne, *Proc. Forum on Ozone Disinfection*, International Ozone Institute, Norwalk, Conn. (1976).
8. Prengle H. W. and C. E. Mauk, "Ozone/UV Oxidation of Pesticides in Aqueous Solution", *Ozone/Chlorine Dioxide Oxidation Products of Organic Materials*, International Ozone Association, (1978).
9. Prengle, H. W., C. G. Hewes, and C. E. Mauk, "Oxidation of Refractory Materials by Ozone with Ultraviolet Radiation," *Proc. Second International Symposium on Ozone Technology*, International Ozone Institute (1975).
10. Prengle, H. W. and C. E. Mauk, *Water-1977 AICHE Symp. Ser.*, **74**, 288 (1978).
11. Prengle, H. W. and N. Barona, *Hydrocarbon Processing* **49**, 159 (1970).
12. Kuo, C. H. *et al.* *AICHE Symp. Ser.*, **73**, 230 (1977).
13. "Standard Methods for the Examination of Water and Wastewater," 14th ed. American Public Health Assn. Washington, D.C. (1975).
14. Prengle, H. W. and C. E. Mauk, *Proc. of Workshop on Ozone/Chlorine Dioxide Oxidation Products of Organic Materials*. EPA/International Ozone Institute, Cincinnati, Ohio, Nov. 16-19, 1976.
15. Kuester, J. and J. Mize, "Optimization Techniques with FORTRAN," McGraw-Hill Book Co. New York, N.Y. (1973).
16. Prengle, H. W., *Environmental Sci. & Tech.*, **17** (12), 743 (1983).
17. Hoigne' J., "Mechanisms, Rates and Selectivities of Oxidation of Organic Compounds Initiated by Ozone in Water." "Handbook of Ozone Technology and Applications," Vol. 1 Rice, R. G., Netzer, A. (ed.) Ann Arbor Science, Ann Arbor, Mich. (1982).

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# The Removal of Trace Levels of Dioxins From Water by Sorption on Modified Clay

Chemical treatments and FTIR measurements have been carried out to help elucidate the binding interaction between Humic acid and modified clay. Partition behavior of surrogate molecules like Octachloro dibenzo-p-dioxin and Hexachloro biphenyl on the synthetic sorbent are examined.

Keeran R. Srinivasan, H. Scott Fogler, Erdogan Gulari, Tim Nolan and Jerome S. Schultz, Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109

Removal of trace organic pollutants like polychlorinated biphenyls (PCBs) and polychlorinated dioxins (PCDDs) from industrial effluent water is a task of utmost importance in order to minimize further contamination of our aquatic environment. Of all the trace organics in water, 2, 3, 7, 8-Tetrachloro dibenzo-p-dioxin (2, 3, 7, 8-TCDD) is believed to be the most toxic [1] and in this paper we describe our preliminary attempts to develop the technology for effective removal of this isomer from wastewater.

Many different approaches have been taken to detoxify 2, 3, 7, 8-TCDD, the most promising and prominent of which are [1]:

- Photolytic dechlorination
- Catalytic degradation using catalysts like RuO<sub>4</sub> and
- Thermal decomposition

An alternative method, eminently suitable for the removal of trace levels of a toxic compound from extremely large volumes of water, is adsorption of the compound on a suitable sorbent which may be subsequently disposed of with relative ease, perhaps using one of the aforementioned techniques.

In this paper, we present the results of our ongoing research to develop a cost-effective, synthetic sorbent based on modified montmorillonite. Chemical modifications and FTIR measurements on the modified clay have been undertaken to probe the nature of the sorbent. Determination of Linear Partition Coefficients (PCs) for the binding of 2, 4, 5, 2', 4', 5'-Hexachloro biphenyl (HCB) and 1, 2, 3, 4, 6, 7, 8, 9-Octachloro dibenzo-p-dioxin (OCDD) to the modified clay has been carried out. These two compounds were chosen as the representative of chlorinated biphenyls and as the structural surrogate of 2, 3, 7, 8-TCDD, respectively. The preliminary results of this study are discussed and the future course of our research delineated.

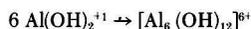
## EXPERIMENTAL

### 1. Selection of the Sorbent

2, 3, 7, 8-TCDD is a rigid, rectangular, nonpolar molecule 1 nm long and 0.35 nm wide with a molecular thickness about the same as its width [2]. A clue to the type of binding interaction expected between TCDD and the sorbent may be inferred from the standard free energy change ( $\Delta\mu^\circ$ ) for the transfer of this compound from water to any nonpolar solvent [3]. The results of such a calculation using liquid-liquid distribution data [4] at 298 K for a

group of organic solvents are shown in Table I. Not unexpectedly, the main driving force behind the sorption of TCDD seems to be the well known Hydrophobic Effect. Similar conclusions were reached by Voice and Weber [5] with regard to PCB sorption by natural sediments, soils, and suspended solids.

It was recognized that Humic Acid (HA), a polyanionic soil organic compound with a hydrophobic core, will be quite suitable as an "ideal" sorbent (both in terms of cost effectiveness and high values of PCs) when irreversibly immobilized on clay with its large surface area per unit mass. Of all the modes of binding between clay and HA, chelate formation between the carboxyl and acidic hydroxyl groups of HA and the edge cations like Al<sup>3+</sup> of the clay would be most stable [6, 7, 8]. Furthermore, pretreatment (or more precisely, cation-exchange) of clay with synthetic polyhydroxy-aluminum compounds is expected to promote chelate formation more easily between HA and the treated clay. As an example, Hydroxy Aluminum (OH-Al) which was originally developed by Dr. Marion G. Reed of Chevron Oil Field Research Corporation may be deemed as prime candidate, since Hydroxy Aluminum is a polynuclear cation formed according to the following reaction [9]:



These positively charged polynuclear cations bind strongly to the interlayer and external surfaces of clay and are virtually nonexchangeable, rendering the kind of stability required of the sorbent.

In summary, clay or montmorillonite would be the substrate of the sorbent which is cation-exchanged either with

TABLE I. PROPERTIES OF 2, 3, 7, 8-TCDD  
(A) Symmetric, Rigid Molecule  
(B) 0.2 ppb Solubility in H<sub>2</sub>O  
(C)  $\Delta\mu^\circ$  (Transfer) from liquid-liquid distribution  
Data at 25°C

Solvent	$\Delta\mu^\circ$ (W - HC)
O-Dichlorobenzene	-56.4 (K. J./mole)
Chlorobenzene	-46.4 (K. J./mole)
Benzene	-36.4 (K. J./mole)
Octanol	-35.5 (K. J./mole)

Clearly demonstrates the hydrophobicity of 2, 3, 7, 8-TCDD. Suggests sorbents with hydrophobic surfaces.

polynuclear cation like OH-Al or polyvalent cations like  $\text{Cu}^{2+}$  or  $\text{Fe}^{3+}$  and HA is finally bound to the clay via this sandwich layer of positive charge. A flowchart outlining the above concept is shown in Figure 1. Concomitantly, HA was directly bonded to hydrated Aluminum Oxide using identical conditions in order to assess the effects, beneficial or otherwise, of using clay as the matrix.

## II Preparation of Sorbents

Na-montmorillonite was obtained from Source Clay Minerals Repository, University of Missouri, Columbia, Mo. Humic Acid was purchased from Aldrich Chemical Co. and Hydroxy-Aluminum (6M OH-Al solution) was a gift from Dr. Marion G. Reed of Chevron Oil Field Research Company. All other chemicals and reagents were analytical grade.

The clay was expanded and washed in de-ionized water following which it was equilibrated with 0.3 M solution of  $\text{Cu}^{2+}$ , or  $\text{Fe}^{3+}$ , or OH-Al. The total amount of these ions was 10-15 fold excess of the CEC of the clay, estimated to be about 1 eq/kg. The modified clay was extensively washed and suspended in 1 mM NaOAc, HOAc buffer, pH = 6.3.

Humic Acid was fractionated by dissolving the commercial grade in 0.1 N NaOH and centrifuging the resultant solution. Precipitate, if any, was discarded and HA was precipitated at pH 1.3 using 1 N HCl and the precipitate collected by centrifugation. This process of dissolution-centrifugation was repeated 3 times and the fractionated HA was taken up in deionized water and extensively dialysed against deionized water using 3500 Daltons MW cutoff dialysis membrane (Millipore Corporation).

The HA concentration was measured as Dissolved Organic Carbon (DOC) with an Oceanography International Corporation Carbon Analyzer (PIR 2000) [10]. Alternatively, it was also measured by OD measurements at 465 nm using DOC analysis to prepare a calibration curve for each batch of HA stock solution. HA is a heteropolymer of a variety of functional groups and its UV-Visible spectrum is a structureless continuum due to the overlap of a multitude

of absorbance bands. In other words the optical density of a HA solution increases monotonically with decreasing wavelength. It has been recognized that the OD at 465 nm, E4, is a valid measure of HA concentration in solution, provided the extinction coefficient at this wavelength is independently established for each batch of HA stock solution using DOC analysis. All OD measurements were made at a constant pH = 8.0. Finally, it was ascertained that the ratio of absorbance at 465 nm to that at 665 nm, namely the E4/E6 ratio, is invariant [11]. It has been shown that the E4/E6 ratio is governed primarily by the particle size and the molecular weight of HA which, in turn, will have an effect on the OD of the solution [12]. Thus, in case of variations in E4/E6 ratios, quantification of HA was done solely by the DOC method.

Isotherms of HA binding to modified clay were constructed by adding increasing amounts of HA in a buffer to a fixed amount of modified clay. From the initial and the equilibrium concentration of HA in solution, the amount of bound HA was estimated. The Hydrated Alumina-Humic Acid complex was prepared by an identical procedure. The following complexes have so far been prepared:

- 1) Clay-HA
- 2) Clay- $\text{Cu}^{2+}$ -HA
- 3) Clay- $\text{Fe}^{3+}$ -HA
- 4) Clay-OH-Al-HA
- 5) Alumina-HA

Each of the above complexes was extensively desorbed in deionized water to remove the reversible component of bound HA, following which the sorbent was air-dried at 333 K and stored for later use.

FTIR spectra of HA in solution or of HA bound to modified clay were obtained by mixing an aliquot of the solution or a known weight of the sorbent with KBr, vacuum drying at 373 K to remove moisture, following which the mixture was pelletized and IR spectra were recorded on a DIGILAB FTS.20C FTIR spectrometer.

## III. Determination of Partition Coefficients

Binding of HCB and OCDD to the sorbent was followed by a radiometric method.  $^{14}\text{C}$ -labelled HCB (24 mCi/m mole or 144 dpm/ng) and OCDD (21 mCi/m mole or 96 dpm/ng) were obtained from Pathfinder Labs., St. Louis, Mo. and used without further purification since the compounds were greater than 98% pure. In the case of HCB, the required amount of sorbate in hexane was transferred to the reaction tube and the solvent (Hexane) allowed to evaporate. Following the evaporation of the solvent, filtered, deionized water, mixed in with the required amount of sorbent, was added to the tube containing HCB to begin the equilibration. In the case of OCDD, the sorbent and water were intimately mixed and the sorbate was injected to start the equilibration. In the latter case, the aqueous solution contained a small amount of the carrier solvent, Tetrahydrofuran (THF). This procedure was used specifically in the case of OCDD since this compound was more soluble in the water-THF binary mixture at ppb levels than in water alone. The highest THF concentration used was 3,000 ppm by vol. and THF is readily miscible in water at these concentrations.

Following overnight equilibration (which was experimentally determined to be sufficient time for the attainment of equilibrium), the sorbent was separated by centrifugation at 1600 g for 45 minutes and an aliquot of the supernatant was counted to give "free" concentration of the sorbate. The sorbent was filtered and the filter pad counted to yield the extent of "bound" sorbate. Finally, the empty glass tube was extracted with scintillation liquid and the amount bound to "glass" was determined. The radioactivity was counted on a Tri Carb Liquid Scintillation Spectrometer, Model No. 2002. Counting efficiency was determined to be around 93% using a sealed  $^{14}\text{C}$  exter-

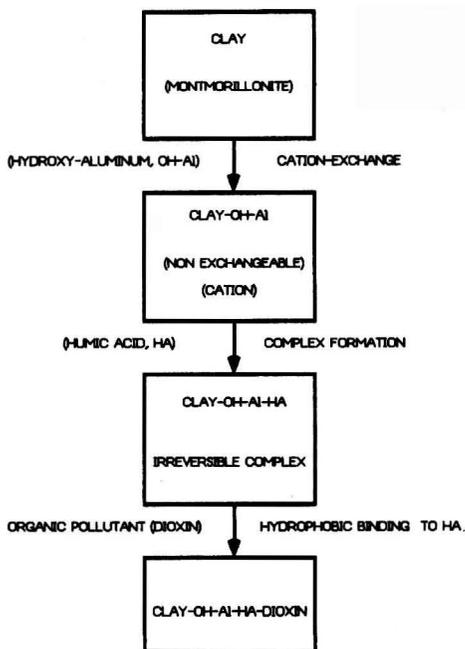


Figure 1. The concept of the synthetic sorbent.

nal standard. Quench corrections, where appropriate, were applied using the Channels Ratio Method [10]. This procedure enabled us to evaluate the mass balance as well as the apparent partition coefficient expressed as:

$$PC = \frac{\text{ng bound sorbate/kg sorbent}}{\text{ng sorbate in solution/dm}^3 \text{ solution}}$$

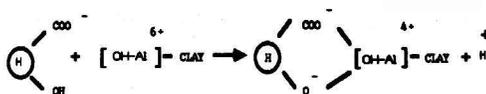
so that the units of PC were dm<sup>3</sup>/kg.

## RESULTS AND DISCUSSION

### I. Nature of HA Binding

The binding of Humic Acid to Clay-Cu<sup>2+</sup>, Clay-OH-Al, and Hydrated Alumina is shown in Figure 2. Clay-Cu<sup>2+</sup> forms the so-called C-type or constant partition type isotherm. Since, at a pH = 6.3, HA is unlikely to penetrate the interlayer space of clay particles, a continuous increase in HA binding sites indicates intercrystalline expansion, i.e., increase in the space between unit cells [13]. This kind of increase has been observed in the case of Ca<sup>2+</sup>, Al<sup>3+</sup>, and Fe<sup>3+</sup> saturated montmorillonite [14]. Of more relevance to the present study is the fact that greater than 80% of bound HA desorbs from Cu<sup>2+</sup> saturated clay upon successive washing with water. A similar instability was also observed in the case of Clay-HA and Clay-Fe<sup>3+</sup>-HA complexes. Such a weak interaction between HA and modified clays precluded their use as sorbents.

Clay-Hydroxy-Aluminum-HA and Alumina-Humic Acid were found to form irreversible complexes. Interestingly, at the lower end of the binding isotherm, where the initial amount of HA is low, the pH of the supernatant following equilibration was seen to decrease, indicating chelate formation between HA and the modified clay or alumina according to the following reaction.



The above mechanism is quite similar to the one proposed by Van Dijk [15] for the reaction between HA and Aluminum ions in solution, and a drop in pH as a consequence of the reaction has been verified both by Van Dijk and others [16]. At the upper end of the isotherm, where saturation occurs, the pH of the supernatant was found to increase. This increase in pH can be rationalized on the basis of Anion Exchange between polyanionic HA in solution and the surface bound hydroxyl or acetate ions on the Hydroxy-Aluminum modified clay at the pH. Figure 2 shows that bound HA reaches an asymptotic value of about 24 g HA/kg modified clay and 18 g HA/kg Alumina.

In order to differentiate between the two modes of binding, chemical modification and FTIR examination of the clay complex were attempted. Modified clay-containing HA was treated for 24 hours with different reagents, indicated in Table 2. The organic carbon content (Humic Acid) was measured prior to and following treatment and the results are summarized in Table 2. The HCl treatment was expected to displace most of the ion-exchange component and, in the case of phosphate, perturbation of both components was anticipated. Finally, 0.1 N NaOH was expected to leach out most of the Humic Acid by dissolving the Hydroxy-Aluminum attached to the clay surface. A second possibility is that, at high pH, Hydroxy-Aluminum undergoes charge reversal and HA will be released from the surface due to electrostatic repulsion. The losses of organic carbon shown in Table 2 coupled with the steep initial slope of HA binding to Clay-OH-Al (Figure 2), suggest that HA is bound equally via ion exchange and chelation to modified clay. The fact that about 20% of HA is still bound to the clay following NaOH treatment indicates that a higher concentration of NaOH or a longer treatment time are necessary to remove all of the HA. In any case, further experiments such as H<sub>2</sub>O<sub>2</sub> oxidation, extraction with strong chelating agents like EDTA, competitive binding in the presence of model compounds, and the effects of ionic strength and pH are contemplated to quantify the extent of chelate formation vs. anion exchange of HA on modified clay.

The FTIR spectra of HA in solution at pH 6.3 and 3.0 (at this low pH some of the COOH groups are expected to be protonated) were compared with the spectrum of Clay-OH-Al-HA. The FTIR spectra of HA alone in solution at

CLAY-Cu, CLAY-OH-Al, and ALUMINA

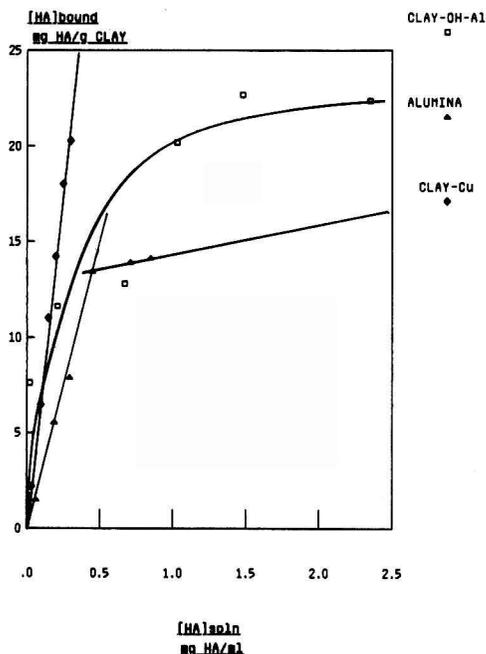


Figure 2. Binding of HA to modified clay.

TABLE 2. CHEMICAL MODIFICATION OF CLAY-OH-AL-HA

Treatment Description	% Carbon Before	% Carbon After	% Loss	Remarks
0.1 N HCl	2.22	1.80	18	Mainly Ion Exchange component removed.
1 M Phosphate Buffer, pH = 6.7	2.22	0.83	63	Ion exchange and Chelate removed.
0.1 N NaOH	2.22	0.42	81	Hydroxy-aluminum dissolved; or charge reversal occurs leading to the loss of HA.

NOTE: For further details refer to text.

pH 6.3 and that of the complex prepared at the same pH are shown in Figure 3 and Figure 4, respectively. In the region of interest, namely  $1720\text{ cm}^{-1}$ , it has been reported [17] that the intensity of bands at  $1720\text{ cm}^{-1}$  (due to C=O stretch of COOH) and at  $1200\text{ cm}^{-1}$  (due to the bending mode of C=O of COOH) are seen to decrease as the chelate is formed and at the same time the companion bands at  $1630$  and  $1400\text{ cm}^{-1}$  (due to C=O stretch of  $\text{COO}^-$ ) grow in intensity. It has been inferred that chelate formation between metal ions and HA in solution leads to such shifts in intensity [17]. From Figure 4, it can be discerned that the band at  $1720\text{ cm}^{-1}$  is totally absent, while the twin bands at  $1630$  and  $1385\text{ cm}^{-1}$  have significant intensity. The band at  $1200\text{ cm}^{-1}$  can not be located due to a shifting baseline. Moreover, part of the intensity at  $1630\text{ cm}^{-1}$  is presumably due to an OH-deformation band of residual water in the complex plus the surface hydroxyls of clay itself. It should be mentioned that the FTIR spectrum alone can not be used to distinguish between anion exchange vs. chelate formation. Not unexpectedly, there is some similarity in the  $1720\text{-}1200\text{ cm}^{-1}$  region of the spectrum between Figure 3 and Figure 4. We have carried out binding experiments between Humic Acid and modified clay at lower pH, where the distinction between the two types of binding may be more obvious, and we have examined these complexes using FTIR. We have also developed an algorithm to straighten the baseline of the observed spectra and have been able to quantify different peaks in the spectra, these results will be reported in a sep-

arate article. In summary, extensive desorption with deionized water, chemical treatments, and FTIR, taken together indicate strong and irreversible binding between HA and modified clay, be it anion exchange type or chelate formation. We have not studied the interaction between HA and Hydrated Alumina in a similar manner. However, irreversible binding of Humic Acid to the extent of 1.8% by weight (Figure 2) leads us to conclude that the same type of binding may be said to occur between HA and Hydrated Alumina.

## II. Determination of Partition Coefficients

Our purpose was to measure Partition Coefficients at as low a concentration of the pollutant as possible. However, the use of the  $^{14}\text{C}$  radiometric method meant that concentrations lower than a few ppb were not practical. The inclusion of THF in the solution phase enabled us to use OCDD at ppb levels.

THF is the carrier solvent in which radioactive OCDD was supplied to us. THF is miscible in water up to the highest volume fraction used in this study (3,000 pm). Since THF is a dipolar molecule, (vapor phase dipole moment of 1.70 Debye) it is expected to have minimal tendency towards micelle formation. Control experiments in water-THF solutions indicated that THF volatilization was minimal as evidenced by invariant "solution" concentration of OCDD for up to 48 hours provided all the steps were carried out under tightly sealed conditions. These

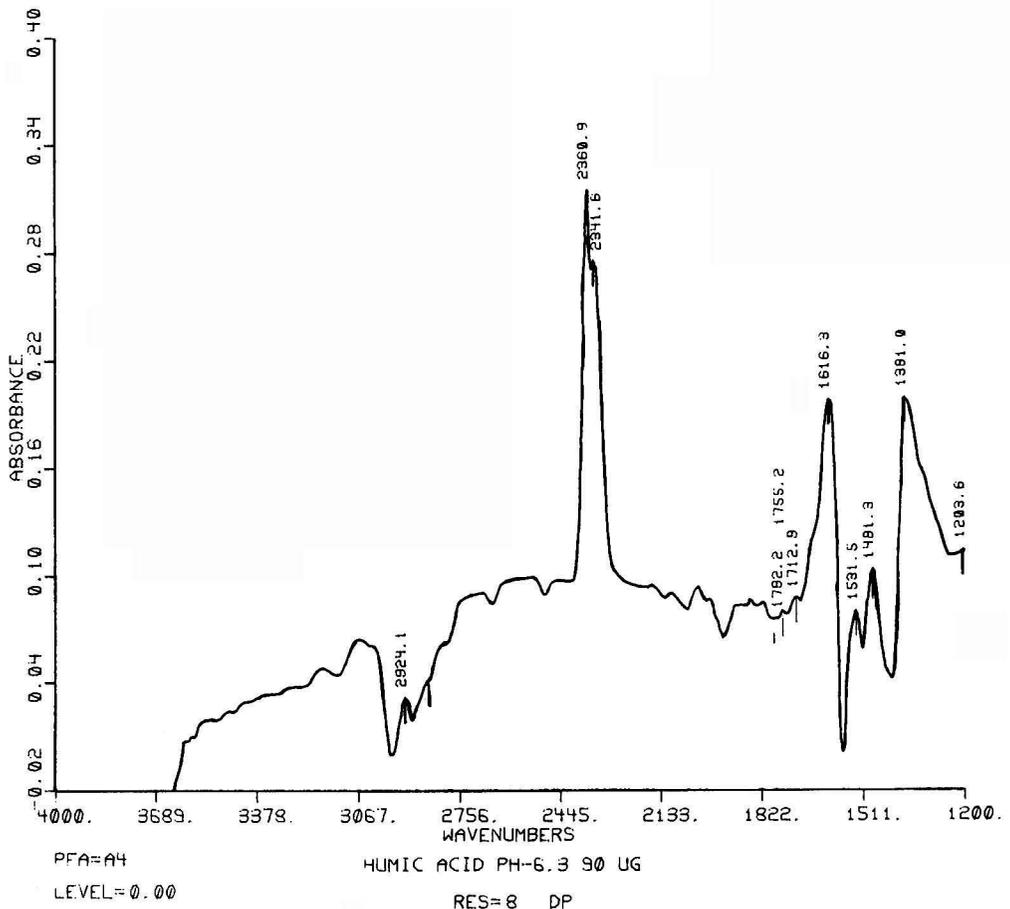


Figure 3. FTIR spectrum of HA at pH = 6.3.

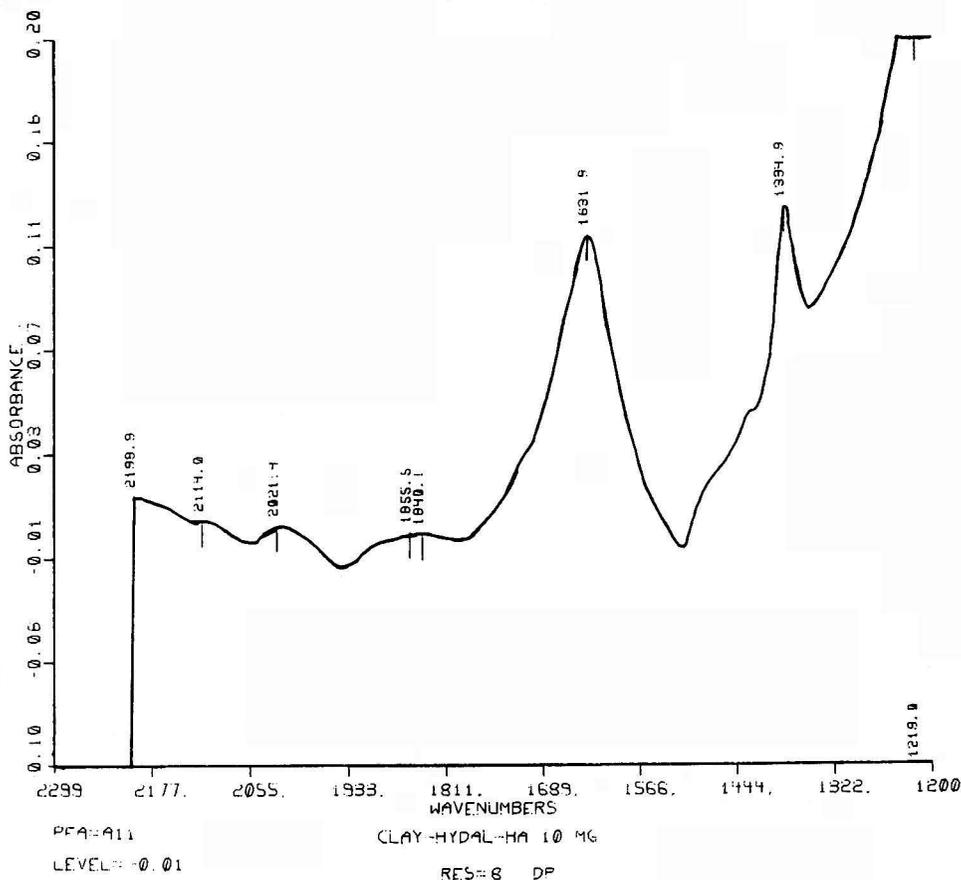


Figure 4. FTIR spectrum of HA on clay-hydroxy-aluminum.

control experiments, i.e., water-THF solution without any sorbent, were performed in duplicate with each sorption experiment to monitor OCDD concentration in solution at the beginning and at the end. It was observed that these two values were within 5% of each other. Centrifugation of a control solution at 1600 g showed no change in OCDD concentration, establishing thereby that there were no large microaggregates. The solution concentration of OCDD measured by this method at different volume fractions of THF is listed in Table 3.

The partition coefficient data for an assortment of clay adsorbents including unmodified montmorillonite and Alumina-HA are presented in Table 4. BET surface areas of all the sorbents listed in Table 4 have been measured and are also included for comparison. A study of Table 4 reveals that the surface area is of greater importance in enhancing binding affinity than the fractional organic carbon content of the sorbent, as has been previously assumed [18]. The basis for this assumption is that sorption of

a hydrophobic molecule on an organic carbon containing solid surface may be likened to the liquid-liquid partitioning of the same compound, as for example between octanol and water. First of all, it can be seen that Clay-Hydroxy-Aluminum-Humic Acid is a better sorbent than unmodified clay, but a dramatic improvement in partitioning behavior is seen with Clay-Hydroxy-Aluminum without any bound organic carbon. The high surface area of Clay-Hydroxy-Aluminum appears to be responsible for the high PC values reported here. Further experiments are under way to elucidate the mechanism of OCDD binding to modified clay sorbents.

TABLE 4. BINDING OF OCDD TO CLAY AND MODIFIED CLAY  
 Sorbent concentration = 0.47 g/dm<sup>3</sup>  
 Volume Fraction of THF = 600 ppm  
 OCDD Concentration = 35 × 10<sup>-7</sup> g/dm<sup>3</sup>

Clay-Compound	% Org. Carbon	Surface Area m <sup>2</sup> /g	PC × 10 <sup>3</sup> g/dm <sup>3</sup>
Clay	< 0.2	27.6	2.0 ± 0.5
Clay-OH-Al-HA	2.2	61.8	7.8 ± 1.8
Alumina-HA	1.8	189.2	17.0 ± 1.0
Clay-OH-Al	< 0.2	114.0	40.0 ± 4.0
Clay-OH-Al & Clay-OH-Al-HA <sup>1</sup>	2.2	—	29.0 ± 3.0

1. The value of PC is based on the combined weight of the two sorbents.  
 ± Indicates the range of PC values from the mean of triplicates. The errors in organic carbon value and the surface area measurement are 0.02 and 5% respectively.

TABLE 3. SOLUBILITY OF OCDD IN WATER-THF BINARY SOLUTIONS

Vol. Fraction THF (ppm)	OCDD Conc. In Solution (× 10 <sup>7</sup> g/dm <sup>3</sup> )
0	~ 1.0
120	40.0
300	62.0
600-3,000	> 70.0

Note: For details of experimental procedure refer to the text.

Preliminary evidence that THF concentration has very little effect on the binding of OCDD to Clay-Hydroxy-Aluminum (not reported here) leads us to believe that the role of THF is one of decreasing the hydrophobicity of the sorbate lower than that of a competitive ligand. The surface area of the sorbent may not be the decisive factor either, since Alumina-HA has a lower PC than Clay-Hydroxy-Aluminum.

Earlier work on the partitioning of PCBs on natural sediments and clays had revealed the existence of so called "Solids Effect" on the apparent PCs [18, 19] i.e., at increasing sorbent concentration, the measured partition coefficient decreases. The non-ideality of the partition behavior has been attributed to:

- a) Increased leaching into aqueous phase of the organic moiety responsible for the binding of the ligand [18].
- b) The presence of an "Implicit," or pre-adsorbed second ligand, which, at high solids concentrations, desorbs from the surface and competes with the test ligand for the binding sites on the surface, lowering the surface excess of the test ligand [20].

In order to verify one of the above possibilities, an equal amount of Clay-Hydroxy-Aluminum was added to Clay-OH-Al-HA and an identical OCDD binding experiment was carried out. If HA was desorbing from the complex, the presence of uncomplexed, modified clay should reverse the process. Comparison of PC values reported in Table 4 (rows 2 vs. 5) shows that the "Solids Effect" is probably insignificant for synthetic sorbents. We are currently investigating this phenomenon in much greater detail and the results will be published in a later article.

Similar experiments with HCB exhibit parallel results and, as indicated in an earlier section, HCB experiments were performed in water without the addition of any organic solvent.

#### CONCLUSIONS AND FUTURE WORK

- 1) Complexes between Clay and Humic Acid can be made irreversible through a sandwich layer of positive charge provided by Hydroxy-Aluminum.
- 2) Humic Acid binds reversibly and in large amounts to  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ -exchanged clay. However, more than 80% of bound Humic Acid desorbs upon washing with de-ionized water.
- 3) The irreversible binding of Humic Acid to modified Clay is due to many factors: nonexchangeability of Hydroxy-Aluminum, chelate formation between bidentate HA and modified Clay, and ion exchange type of binding.
- 4) Partition Coefficients as high 40,000 have been obtained using Clay-Hydroxy-Aluminum.

The results reported here have raised many questions, some of which may be answered by experiments currently in progress. For example, we have been able to prepare a series of clay complexes with organic carbon content ranging from 1.9% to 8.6%. In our opinion, this will enable us to investigate more fully the effect of organic carbon. Secondly, we have discovered that Clay-Hydroxy-Aluminum complex is a potent sorbent of OCDD and HCB. Partition Coefficients in the range of 40,000-80,000 have been obtained without the "Solids Effect." Characterization of the sorbents in terms of their surface areas, surface potentials crystalline states, and CECs is being carried out to help explain the strong affinity of OCDD and HCB for Clay-Hydal. Finally, binding of 2, 3, 7, 8-TCDD to all the different sorbents prepared so far including Clay-Hydal will be studied to confirm the findings obtained with surrogates.

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#### LITERATURE CITED

1. Exner, J. H. "Detoxification of Chlorinated Dioxins," Abstract, ACS Symposium, 186th National Meeting, Division of Environ. Chemistry 23(2), p. 30 (1983).
2. Poland, A. and J. C. Knutson, "2, 3, 7, 8-Tetrachlorodibenzo-p-Dioxin and Related Halogenated aromatic Hydrocarbons: Examination of the Mechanism of Toxicity," *Annual Rev. Pharmacol. & Toxicol.* 22, 517 (1982).
3. Tanford, C. "The Hydrophobic Effect," John Wiley & Sons, p. 4 (1973).
4. Robbins, L. Private Communication, Dow Chemical Company, Michigan Division, Midland, Mich.
5. Voice, T. C. and W. J. Weber, Jr. "Sorption of Hydrophobic Compounds by Sediments, Soils and Suspended Solids," *Water Research* 17, 1433 (1983).
6. Mortland, M. M. "Clay-Organic Complexes and Interactions," *Adv. Agronomy* 22, 75 (1970).
7. Greenland, D. J. "Interaction between Humic and Fulvic Acids and Clays," *Soil. Sci.*, 111, 34 (1971).
8. Theng, B. K. G. "The Chemistry of Clay-Organic Reactions," Adam Hilger (London), p. 291 (1974).
9. Reed, M. G. "Stabilization of Formation Clays with Hydroxy-Aluminum Solutions," *J. Pet. Tech., Trans. AIME*, 253, 860 (1972).
10. Landrum, P. F., S. R. Nihart, B. J. Eadie, and W. S. Gardner, "Reverse-Phase Separation Method for Determining Pollutant Binding to Aldrich Humic Acid and Dissolved Organic Carbon of Natural Waters," *Environ. Sci. & Technol.*, 18, 187 (1984).
11. Schnitzer, M. and S. U. Khan, "Humic Substances in The Environment," Marcel Dekker, New York, p. 62 (1972).
12. Chen, Y., N. Senesi, and M. Schnitzer, "Information Provided on Humic Substances by  $E_4/E_6$  Ratios *Soil. Sci. Soc. Am. J.* 41, 352 (1977).
13. Ref. 8, page 297.
14. Levy, R., and Francis, C. W., "Adsorption and Desorption of Cadmium by Synthetic and Natural Organo-Clay Complexes," *Geoderma* 15, 361 (1976).
15. Dijk, H. Van, "Cation Binding of Humic Acids," *Geoderma*, 5, 53 (1971).
16. Ref. 11, page 225.
17. Schnitzer, M., 9th Intl. Congr. Soil. Sci. Trans., Adelaide, Australia, 1, 635 (1968).
18. Voice, T. C., C. P. Rice, and W. J. Weber, Jr., "Effect of Solids Concentration on the Sorptive Partitioning of Hydrophobic Pollutants in Aquatic Systems," *Environ. Sci. & Technol.* 17(9), 513 (1983).
19. O'Connor, D. J. and J. P. Connolly, "The Effect of Concentration of Adsorbing Solids on the Partition Coefficient," *Water Research*, 14, 1517 (1980).
20. Curl, R. and G. Keolian, "An Implicit-Adsorbate Model for Apparent Anomalies with Organic Adsorption on Natural Adsorbents" *Environ. Sci. & Technol.* 18(12), 916 (1984).



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# Design and Operating Problems of Hazardous Waste Incinerators

**In selection of an incinerator unit it is extremely important to review the experience of a particular design for the service for which it will be used.**

Joseph J. Santoleri, Four Nines, Inc., Plymouth Meeting, Pa.

The proper and continuous operation of an incineration system for hazardous wastes has become a major responsibility of the plant engineer. The Resource Conservation and Recovery Act (RCRA) established the final requirements for incinerators on July 21, 1982. Owners and operators of incinerators had to submit completed applications for Part "B" of the operating permit by the end of 1983. This established the recording and monitoring procedures necessary to insure that their operation is within approved parameters.

Typical problems associated with operating a hazardous waste incinerator on an around-the-clock basis are covered in this paper. Areas of concern are: waste liquid handling (pumps, piping, and control valves); waste liquid atomization; refractory maintenance; instrumentation and analysis equipment; waste heat boilers; and air pollution control systems. Failures in the system cause shutdowns of not only the incinerator but also the process which generates the waste. This becomes serious when production (cash flow) is curtailed. Proper and scheduled maintenance will reduce these problems and provide 95+% on stream time.

## PROBLEM EVALUATION

An estimated 57 million metric tons of industrial hazardous wastes were produced in the U.S.A. in 1980. Many of these wastes are incinerable. Incineration is becoming one of the principal methods used to manage hazardous waste. A better understanding of state-of-the-art incineration technology is important to the plant engineer responsible for hazardous waste management. Important in this technology are techniques needed to minimize down-time and maintenance for systems operating on a continuous basis. Close scrutiny during the design stages of a project can prevent subsequent problems. Sophisticated controls and instrumentation are now available for proper operation. Diligent maintenance must become a part of their daily routine.

An incineration system for hazardous wastes must be well designed, instrumented, operated, and maintained as though it were a process system. Plant management must be prepared to provide adequate capital and operating funds for these units. Hazardous waste incinerators are important not only for continuous operation but also for good community relations. Operating units must meet local, state, and federal codes (Resource Conservation and Recovery Act, July 1982). As more systems are installed to provide reliable, safe, long term operation and performance, the public will begin to accept incineration as a safe system to have in its backyard. It is important to understand those problem areas which may cause nuisance shutdowns and provide front page news. Such sensational

news coverage, accurate or otherwise, is damaging to industry [1].

Although this discussion focuses on problems related to the pumpable liquid wastes burned in liquid injection units, the concepts developed can be applied to other incineration units such as rotary kilns, multiple hearth furnaces, fluid bed combustors, and other incineration systems.

## MATERIALS HANDLING PROBLEMS

In the transport of liquid wastes or slurries to the incinerator, the key elements are the storage facility, transfer and feed pumps, metering, control and shutoff valves, and the atomizer. Wastes vary from highly aqueous materials with organics and ash (typical of pharmaceutical and agricultural process wastes) to viscous tars such as toluene diisocyanate with a viscosity of 4500 SSU at 300°F (Figure 1).

The transport system should be designed to prevent blockage in the lines due to waste shutoff to the incinerator, pump failure, or inadvertent shutdown of waste feed to the system. A system handling waste with the following characteristics will cause blockage in a short period of time if improperly designed or operated:

1. A waxy solid or slurry at room temperature.
2. A waste that solidifies if overheated (polymerization).
3. A waste that crystallizes due to evaporation of water.
4. A waste whose temperature is not controlled to produce a clear liquid flow.

With the above material, the original system plugged frequently. The material was heated in the storage tank to 210-225°F. When flow was generated in the piping system, cold pipes absorbed heat from the fluid, cooling it below its solidification point, which caused immediate blockage. Initially, the entire blocked zone had to be removed with the solidified waste in piping and valves. Adding steam to the lines did not open the system. The system was made to operate satisfactorily by preheating the line with steam prior to introduction of the waste. However, this was unsatisfactory when either the steam supply or the waste flow to the nozzle was cut off. By adding a recycle connection to the system as close to the atomizer as possible with close control of the pipe temperature, shutdowns are minimized. Good design with proper operating procedures will permit this system to operate satisfactorily for long periods of time. With this type of waste, the waste should be fed directly to the transport system from the process. If storage is required in the circuit, waste must be maintained at proper temperatures with recirculation designed to provide good mixing in the tank without stratification [2].

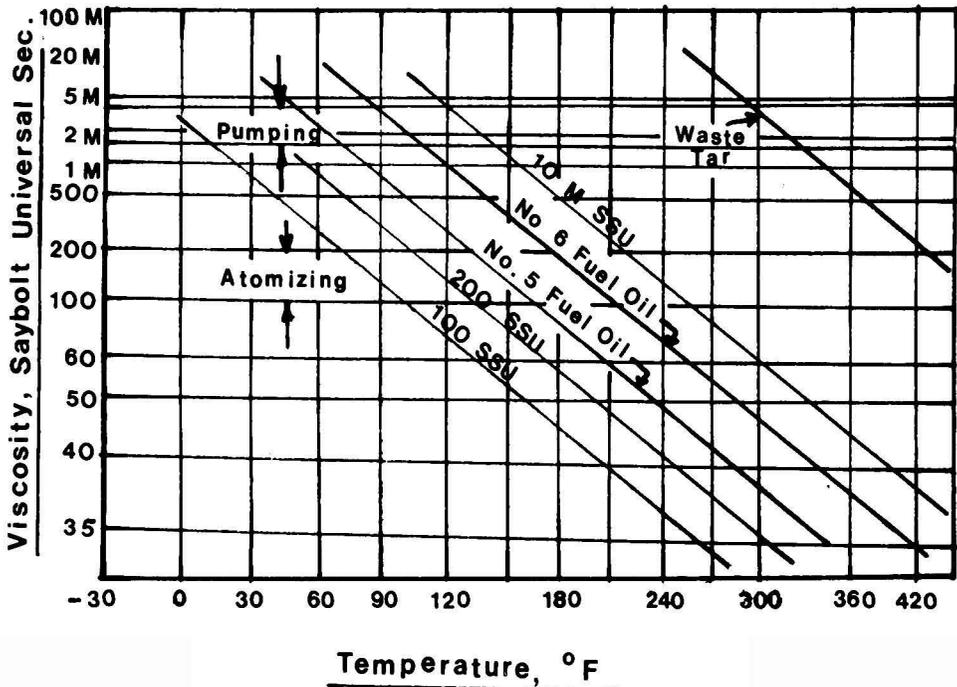


Figure 1. Viscosity-temperature chart.

**Design Procedures: (Figure 2)**

1. High flow rate pump with recycle to storage tank.
2. Direct feed to atomizer as short as possible.
3. Provisions for immediate flushing of lines and good drainage.
4. Proper instrumentation and equipment for controlled heating of lines.

**Operating Procedures**

1. Heat entire system including atomizer with steam, hot water or a fuel oil, at the same temperature as that needed for the waste fluidization.
2. Feed waste into system and allow entire system, including recycle lines and tank, to fill up with waste at a controlled temperature level.

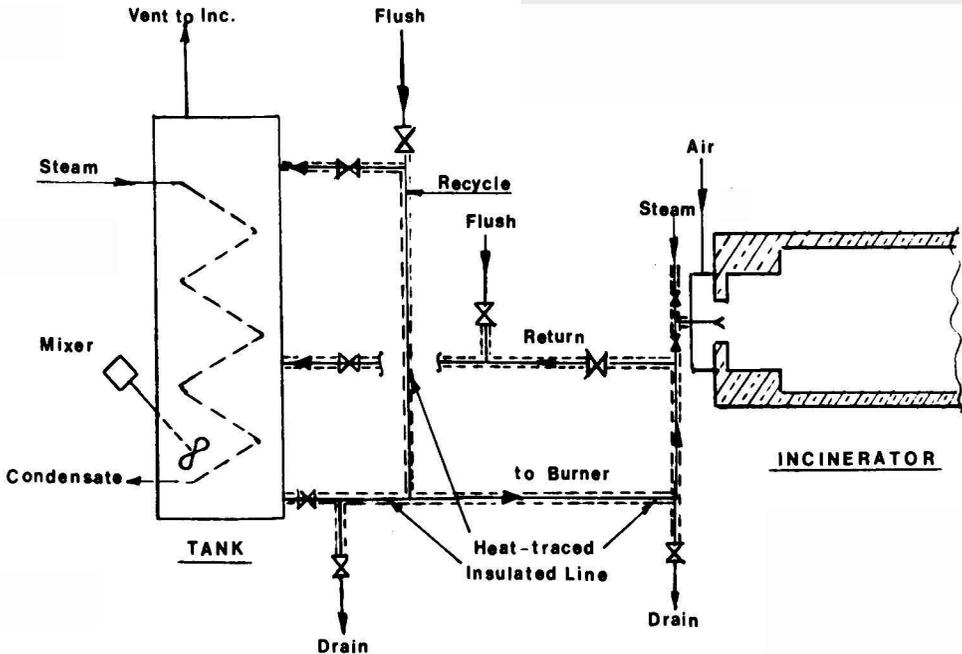


Figure 2. Waste piping system.

- Increase flow rate to maintain velocity in lines at least 3 ft/sec. (Pump size should be adequate to promote flow into minimum 3/4 in. dia. pipe size.)
- Open waste line to atomizer full open.
- Control feed rate to atomizer by flow control on return line to tank.
- Differential flow in lines is flow to atomizer.
- On shutdown, close lines to atomizer.
- Flush lines with hot water or steam and send waste to storage tank.
- Flush atomizing fluid line.
- Drain all connection points after flushing.

### STORAGE PROBLEMS

Aqueous wastes often stratify in the storage tank. An average waste composition might be 95% water, 5% organics and salts. Such waste could be injected into the incineration chamber through spray nozzles downstream from the auxiliary fuel burner. Air is normally supplied at this point, providing at least 25% excess for the organic waste components. The burner is designed to fire the necessary auxiliary fuel with combustion air to maintain an 1800°F chamber temperature.

During startup, a particular unit operated as designed with a waste flow rate of 25 gal/min, with the auxiliary fuel flow (#6 fuel oil) at rating. Within a few weeks after startup, the plant engineer complained about a layer of black oily material in the quench chamber water. The system was as shown in Figure 3, with a submerged quench tank (Sub-X). Everyone at the plant was concerned that the water sprays were quenching the flame and causing incomplete combustion of #6 fuel oil. New nozzles were then supplied with a variety of spray angles and shapes (hollow cone, solid cone, flat spray). There was also concern that the hydraulic nozzle design was not giving a fine droplet size. A two-fluid nozzle using compressed air for atomization was tried. All of these were to no avail. A layer of black liquid prevailed on the surface of the water in the quench tank.

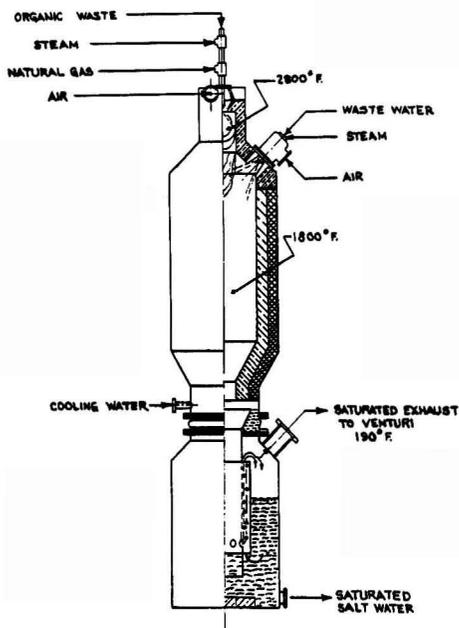


Figure 3. Sub-X incinerator.

Analyses were made of the entering waste and the exhaust gases leaving the incinerator. Samples of liquid were taken during a three day run. The aqueous waste varied from 0% hydrocarbons (HC)-100% H<sub>2</sub>O to 60% HC-40% H<sub>2</sub>O. The waste was produced by various processes throughout the plant. The results indicated that upsets in the process caused a high hydrocarbon loading which caused layering in the storage tank. The tank did not employ a mixing or recycle system. As the organic layer entered the nozzles to the incinerator, a sudden increase in temperature results. The main burner firing rate was reduced to its low firing rate (3:1 turndown). However, the total air supplied to the incineration chamber could not supply oxygen adequate to oxidize the organics. The result was a very rich burning condition which caused unburned organics to enter the quench tank.

The addition of mixers to the main storage tank and a day tank between the main storage tank and incinerator permitted better control of the supply system to the incinerator. There was no longer a sudden surge of high organic content waste to the incinerator. Instead, there was a gradual change in waste composition which could be handled by the incinerator control system. Good mixing provided a waste stream which was much closer to the design specifications.

The switch to the two fluid atomizer permitted nozzles to be turned off during operation without danger of overheating. The previous hydraulic nozzles had no such protection when the flow was turned off. This change has allowed a higher turndown for the total system [3].

Similar problems have been noted in the operation of solid waste incinerators where finely divided organic materials are batch loaded into the incinerator. Scheduled loadings at lower weight levels have improved the operation and minimize the combustion pulse which typically occurs.

### ATOMIZER DESIGN

In any system where atomizers are used to inject waste, either directly through the main burner or into the incinerator chamber, provisions should be made to change the nozzles during operation. A nozzle that has eroded will not provide a good spray pattern or droplet size. Instead, a stream of liquid will form, causing direct impingement on the refractory surface with subsequent failure. Most incinerators operate on a continuous basis at the maximum rate necessary to burn off the waste liquids being generated. Nozzles should inject the waste liquids with the minimum practical droplet size. The better the atomization the smaller the droplet and the more rapid the combustion or oxidation (Figure 4).

Since atomization is critical to the operation of an incinerator, it is important that a review of the atomizer be made in the initial design. Selection should be based on the viscosity of the waste liquid, ash content (%), and physical properties (size, density, abrasion characteristics), reactions with other streams (water or steam, other wastes, fuels) and total flow rate. The number of atomizers and their location in the incineration chamber is also important to good distribution [4].

### ATOMIZER LOCATION

A recent incinerator operation problem was determined to be nozzle size and location. The nozzle type was correct for the type of waste. It was an external atomizing type using steam as the atomizing fluid (Figure 5). The problems were the quantity of waste being injected through each nozzle and the locations of these nozzles with respect to the primary burner. As flow increases in a nozzle, the nozzle flow design requires that the area must also increase to maintain the velocities of the waste liquid and

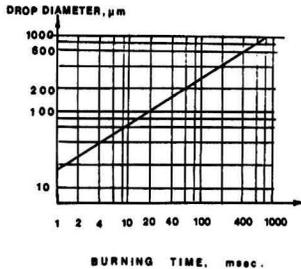
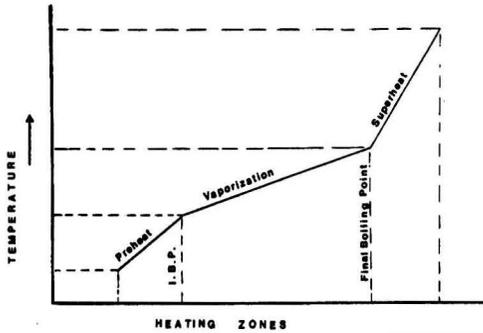


Figure 4. Droplet vs. burning time.

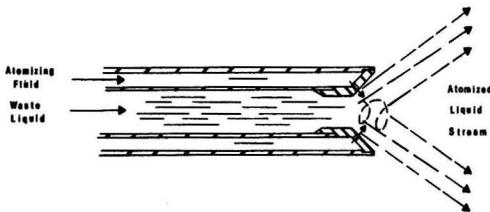


Figure 5. External atomizer nozzle.

atomizing fluid. As the diameters increase, it is difficult to maintain a droplet size in the 100-150  $\mu$  size range required for rapid oxidation. With larger droplets it is also more difficult to provide good mixing of combustion air with the droplets for the length of time needed to evaporate, superheat, and oxidize the waste. As a result, there was impingement of these liquid droplets on the refractory walls, and the droplets reagglomerated into a stream of liquid which became much more difficult to burn.

#### Nozzle Design (Table 1)

As an example, a 3.3-gal/min nozzle requires an orifice of .45 in. for a 3-ft/sec velocity. A 10-gal/min nozzle needs a 1-3/8 in. orifice for the same velocity. The atomizing fluid in the 10-gal/min nozzle must penetrate a thicker stream of liquid. The 3.3-gal/min nozzle forms an average particle

TABLE 1. COMPARISON OF NOZZLE DESIGN

	10 GPM	3.3 GPM
Orifice Dia.	1.375 in.	0.45 in.
Droplet Size	300 $\mu$	125 $\mu$
No. of Droplets	44,200	610,700
Droplet Surface Area, $\text{cm}^2$	125	300

size of 125  $\mu$  and the 10-gal/min nozzle form droplets with a particle size of 300  $\mu$ . Three 3.3-gal/min nozzles will produce 610.7M droplets with a surface area of 300  $\text{cm}^2$ . The single 10-gal/min nozzle produces 44.2M droplets with a surface area of 125  $\text{cm}^2$ . With three 3.3-gal/min nozzles located as shown in Figure 6, the heat transfer rate from the high temperature products of combustion to the droplets will be much more rapid than to the larger droplets from the 10-gal/min nozzle and evaporation will be more rapid. (Ratio is 2.4:1) [5].

The single 10-gal/min system was much less expensive to install, but it did not produce the desired results. The nozzle was also directed too close to the main flame, quenching combustion from the main auxiliary fuel burner, adding to the problems of the incinerator.

#### Oxidation Air

Important in the design of liquid waste incinerators is the supply of combustion and secondary air and the injection point with respect to the wastes. Waste injected directly into a combustor is usually supplied with primary air. The two streams are well mixed in the combustion process (Figure 7). However, there are systems where waste is injected directly into an incineration chamber. The oxygen needed for combustion of the organics comes from either excess air from the main burner (Figure 8) or as air leakage, typical in rotary kilns. As a result, the organics are being vaporized and superheated without the proper oxygen for combustion. To properly oxidize a waste liquid, the hydrocarbons should be in a gaseous state mixed with an excess of air or oxygen to promote rapid oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  vapor. If oxygen is not available, the hydrocarbons will be pyrolyzed to  $\text{CO}$ ,  $\text{H}_2$ , and soot. Then, addi-

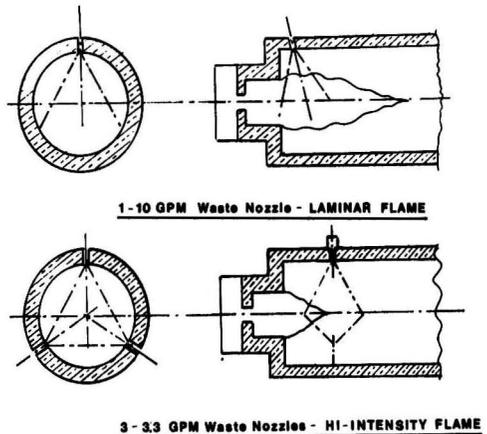


Figure 6. 3-3.3 gal/min nozzles vs. 1-10 gal/min nozzle.

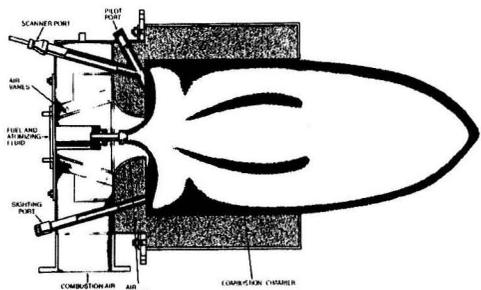


Figure 7. Vortex burner. Reproduced by permission of Trane Thermal.

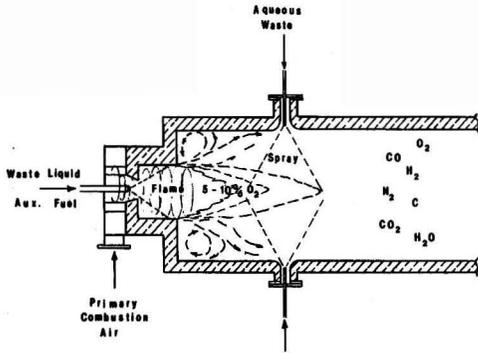


Figure 8. Aqueous waste incinerator without secondary air.

tional residence time to insure complete oxidation is necessary, providing sufficient oxygen is available. In many cases this does not occur, and the pyrolyzed products coat the refractory walls and leave the chamber as unburnt soot particles.

In one installation (Figure 9) a nightly shower of sparks came from the incinerator as deflection of the stack occurred from temperature differential and wind effects. Figure 10 shows why a hydrocarbon will not be oxidized in a low oxygen environment. This is covered in more detail in [6].

By proper design of the oxidizing air system (Figure 11) the incinerator was able to operate more efficiently. The burner could now be operated at 5-10% excess air, which provided a much higher flame temperature. The available heat at the 1800°F incineration temperature increased from 37% to 50% (Figure 12).

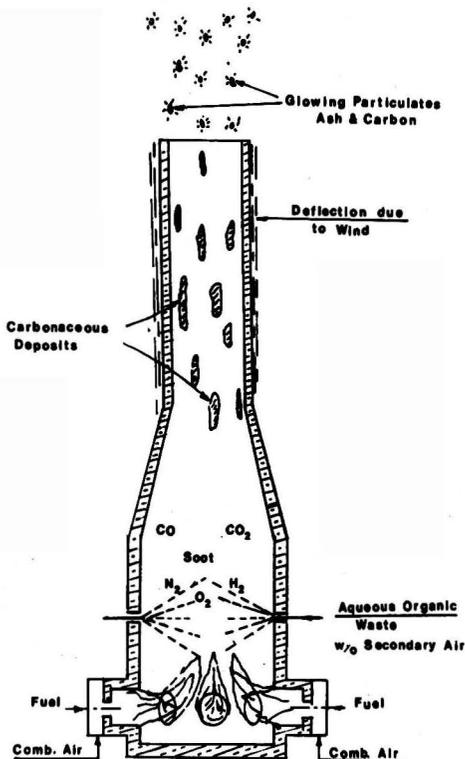


Figure 9. Vertical incinerator w/o secondary air.

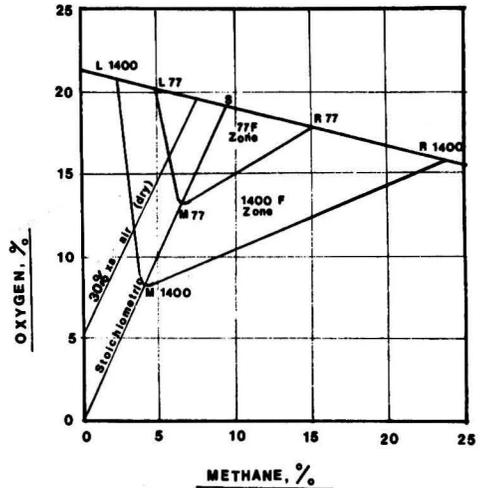


Figure 10. Flammable zones—methane vs. oxygen.

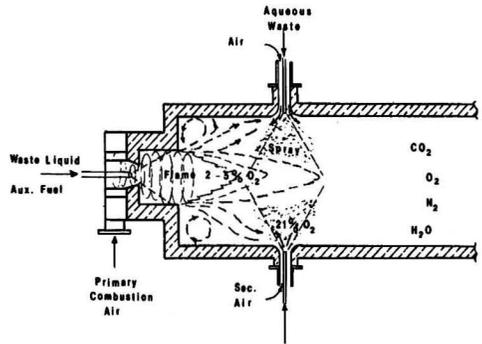


Figure 11. Aqueous waste incinerator w/secondary air.

For a system operating with a required heat input to the waste of 25 MM Btu/hr., the auxiliary fuel (natural gas) with 5% excess air is 50 MM Btu/hr vs. 67.5 MM Btu/hr at 40% excess air. At fuel costs of \$5 per 1000 CF of natural gas, this savings equates to \$700,000 per year (8,000 hr operation). At the same time, the problems associated with pyrolysis products exiting the stack have been eliminated.

Consideration should be given in any system to utilizing compressed air for atomization rather than steam. The air is supplied either from a blower or fan. If steam is used, it must also be raised to the incineration temperature. For a waste rate of 10 gal/min approximately 1670 lbs/hr of steam is required for atomization. The auxiliary fuel needed to raise the steam to temperature is 2 MM Btu/hr. This must be supplied by the total system. With compressed air for atomization, this additional fuel can be saved because the air takes part in the combustion reaction.

These are a few of the problems that have been observed in incineration systems that have been placed into operation. Users of this equipment who follow the operation closely have been able to provide valuable input for improvements that are needed to reduce failures in high temperature waste incineration systems. Manufacturers who follow the performance of equipment that has been placed in the field also have made many improvements in design and control.

These improvements have resulted in capital cost increases to the original equipment; however, they have caused a marked reduction in the operating costs of these

All curves for hot air are based on 10% excess air.  
All curves for excess air are based on 60 F temperature.

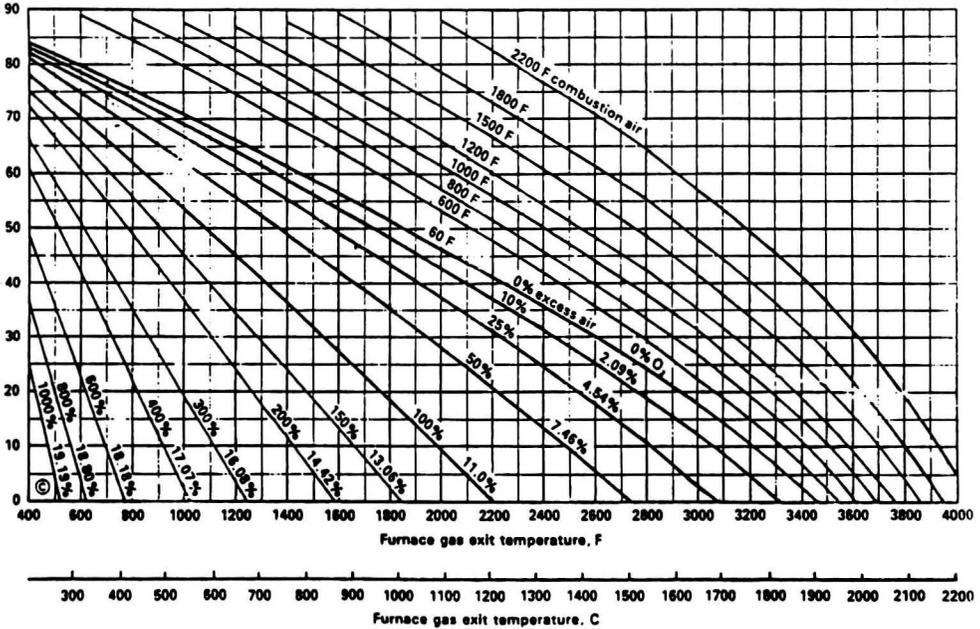


Figure 12. Heat availability chart. Reproduced by permission of North American Mfg. Co., Cleveland, OH.

units that do, in fact, have quality design and controls. With these improvements, users will now schedule preventive maintenance on the equipment, resulting in less downtime [7, 8, 9, 10].

Systems that had been purchased on price alone have made second time users look closely at all costs, capital and operating. For examples: a system priced at  $\$1.4 \times 10^6$  was selected over one costing  $\$1.2 \times 10^6$  (a  $\$200,000$  premium) based on the savings the user had projected would result from lower maintenance. With a similar lower cost system, his past experience indicated that refractory maintenance alone would result in an annual cost differential of over  $\$50,000$ . This did not include the fuel savings, nozzle replacement costs, downtime costs, etc [11].

It is extremely important in the installation of a new incinerator unit or in retrofitting an existing system to review the experience of a particular design for the service for which it will be used. In many cases, the purchaser does not question past experience and the final decision is based only on total installed costs and the manufacturer's guarantee of performance.

With today's high cost of fuel and labor, operating and maintenance costs play a large role in the total annual cost of a system (Table 2). By checking on similar systems with reasonable operating experience a true bid evaluation can be made. It is worth the time to visit installation sites and discuss operating problems with the owner and his plant personnel. This is most important as part of the bid review

procedures. Systems that have overcome initial design and operating faults will go a long way in providing long term operation in the process plant.

#### LITERATURE CITED

1. Resource Conservation and Recovery Act. Standards for Owners and Operators of Waste Facilities: Incinerators. 40CFR264, RCRA 3004, Jan. 25, 1981, Rev. July 21, 1982.
2. Personal Communications with R. Johnson, Virginia Chemical Co.
3. Personal Communications with American Cyanamid Co., Inc., Hannibal, Mich.
4. Santoleri, J. J. "Hazardous Liquid Waste Disposal: Incineration — The Ultimate Solution." National Conference on Hazardous Wastes and Environmental Emergencies, March 12-14, 1984, Houston, Texas.
5. Santoleri, J. J. "Spray Nozzle Selection," *Chemical Engineering Progress* (Sept. 1974).
6. Monroe, E. S. "Incineration of Aqueous Wastes," ASME National Incineration Conference, May 1968.
7. Ready, D. F. and R. F. Schwab, Allied Chemical Corp., "Incineration Problems and How to Prevent Them," *Chemical Engineering Progress* (Oct. 1980).
8. Olson, D. A. and R. J. Nebrbauer, Merck & Co., "Off-Gas Incineration with Emissions Control," Pharmaceutical Manufacturers' Association Spring Meeting, April 1983, Kalamazoo, Mich.
9. Tipps, W. M. "Incinerating Cutting Oils and Similar Liquid Effluents Without Polluting the Air," 23rd National Plant Engineering Conference, Jan. 1972, Philadelphia, Pa.
10. Bernadiner, M. N. et al. "Thermal Methods of Disposing of Industrial Waste Waters from Chemical Plants," *Int'l. Chemical Eng.* 13, No. 2, April 256-263 (1973).
11. Personal Communications with E. Andreacola and G. Irrgang, Trane Thermal.

TABLE 2. COMPARISON OF TWO INCINERATION SYSTEMS

Manufacturer	A	B
Base Price (Equipment)	\$1,200 MM	\$1,400 MM
Annual Operating Costs		
Fuel	\$2,700 MM	\$2.00 MM
Power	\$50,000	\$75,000
Caustic	\$160,000	\$80,000
Maintenance	\$100,000	\$50,000
Total	\$3.01 MM	\$2,205 MM
Differentials		
Base Price		+\$200,000
Operating Costs (Annual)	+\$805,000	



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He is a member of AIChE, ASME, American Society for Testing Materials, Air Pollution Control Association, and the American Gas Association.

# Effect of Ozonation and UV Irradiation on Biorefractory Organic Solutes in Oil Shale Retort Water

The organic solutes in oil-shale retort waters are found to be extremely refractory to both chemical and microbial oxidation alteration or modification.

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Biological treatment of retort water from Occidental Oil Shale Company's modified *in-situ* retort burn #6 (Oxy-6) is initially limited by the endogenous inorganic orthophosphate concentration [1, 2]. Paradoxically, the nutrient that subsequently limits microbial growth is carbon, even though repeated studies have shown that about one half of the dissolved organic carbon (DOC) remains after exhaustive biological treatment [2]; the addition of trace elements does not elicit further growth or DOC removal. Secondary growth is observed, however, when these same cultures are supplemented with an exogenous source of easily degradable carbon such as aliphatic carboxylic acids [2]. Nitrogenous and oxygenated heterocycles and aromatic amines have been implicated [3] as the major chemical classes accounting for the extraordinary recalcitrance of organic carbon in the extracellular fluid that remains (i.e., spent retort water) after exhaustive biooxidation of retort water. This hypothesis has been strengthened by several reports on the chemical characterization of Oxy-6 retort water extracts [4] that indicate the presence of perhaps hundreds of species of aromatic amines and unsaturated, oxygenated nitrogen heterocycles, each at a low part-per-million concentration.

Successful treatment of oil shale wastewater undoubtedly will require the use of more than one pollution control technology. A particular method may be extremely effective for the removal of a specific class of organic compounds, but when applied to a heterogeneous mixture such as retort water, the method may be able to remove only a fraction of the contaminative solutes. Extensive treatment of these waters will require a combination of methods that yield complementary or enhanced performance when used in sequential or simultaneous application. The integration of these processes should be evaluated carefully because the final degree of treatment can be additive (i.e., the sum of the individual processes), synergistic (i.e., greater than the sum of the processes), or antagonistic (i.e., lower than any one of the processes).

Ozonation and ultraviolet (UV) irradiation treatment technologies were investigated for their abilities to augment or enhance the biological treatment of oil shale wastewaters by mineralizing or by oxidatively altering organic solutes that are biorecalcitrant or bactericidal. Alternatively, these two oxidative processes could possibly hinder biooxidation by (i) producing toxicants, (ii) polymerizing solutes that would ordinarily be biode-

gradable, or (iii) creating a multitude of new solutes, each present at a low concentration; the latter possibility would amplify the already existing problem of threshold concentration effects. The effects of ozonation and UV irradiation also can be used as a predictor of the maximum capability of aerobic biooxidation that is effected through oxygenases [5]. Furthermore, the extent of oxidation that results from UV irradiation can give an indication of the degree of liquid and surface phase photolysis that may occur during codisposal of these waters with spent shale or during ponding. Photolysis would probably be the primary route of chemical alteration in the semi-arid tristate region of Colorado-Wyoming-Utah, which experiences less attenuation of ultraviolet energy because of its relatively high elevation and number of sunny days.

## THEORY

### UV Radiation

Irradiation by UV light may complement biotreatment by mineralizing the recalcitrant organic solutes. The degradation of organic solutes by exposure to UV radiation is accomplished by: (i) direct absorption of sufficient UV radiation to cleave intramolecular bonds, producing lower-molecular-weight fragments, (ii) generation of organic free radicals, (iii) interaction of free radicals with oxygen to produce peroxy and hydroperoxy radicals, which are capable of structurally altering or completely mineralizing the lower-molecular-weight fragments by oxygenation, hydrogen abstraction, or by the initiation of radical chain reactions [6, 7, 8]. The primary result of these reactions is to introduce oxygen onto electrophilic carbon of organic molecules; the products of these reactions are more oxygenated, polar, and biodegradable [9]. In addition, it has been shown that the photolysis of endogenous organic compounds in natural waters generates hydroxyl radical (OH $\cdot$ ) and singlet oxygen, which are capable of subsequent transformation of synthetic organic solutes [10].

In contrast to direct mineralization, a more efficient use of UV irradiation may be as an aid to biooxidation; the oxygenation of complex refractory solutes or the production of low-molecular-weight products by UV irradiation may make otherwise resistant molecules available for subsequent microbial attack [9]. This phenomenon has been implicated in the environmental degradation of pesticides [6], in the biodegradation of certain synthetic polymers

[11], and for the destruction of toxic wastes [12]. Photooxidation of a given compound can produce a family of products, each of which may vary in its susceptibility to microbial metabolism [13]. The production of a plethora of oxidation products would be especially significant with respect to oil shale wastewaters. Two factors that probably exacerbate the refractory nature of the substituted heterocyclic compounds in spent retort water are 1) the presence of numerous homologs and variants, each of which may require a specialized catabolic enzyme system and 2) the low individual heterocycle concentrations (see [4]), which are sufficiently below the affinity or threshold values of the requisite catabolic enzymes. Although photooxidation may generate products that could (under the proper conditions) be more easily degraded, it could actually exacerbate the existing problems associated with enzyme specificity and threshold concentration effects.

The direct absorption of energy by chemical bonds is not the only route by which UV radiation can structurally alter organic compounds. An appropriate chromophore or photosensitizer (such as riboflavin) can absorb light energy and transmit the energy to a species that is ordinarily nonabsorbing during its return to the unexcited state. Dye-sensitized energy transfer represents a highly specific means of introducing oxygen into an organic compound [14], and the resultant dissociation products may differ significantly from those of direct photolysis [8].

Molecular oxygen, itself, may be photochemically excited to a highly active state. The result of photosensitized energy transfer stimulated by near-UV irradiation of molecular oxygen is the highly reactive species singlet oxygen [6]. In certain instances, singlet oxygen has been documented as the oxygenating species common to both metabolism and photolysis. A key function of metalloenzymes is, in theory, to induce singlet oxygen generation [6]; the oxygenation chemistry for several classes of oxygenases resembles the reactions of singlet oxygen [14]. Therefore, the degree of mineralization or alteration of organic carbon mediated by the photochemical effects of singlet oxygen may serve to predict the potential of microbial metalloenzymes; that is, if the appropriate enzyme system were available and if it could function in the defined environment, then the action of photochemical oxidation by UV irradiation may mirror the maximum effects that could be achieved by microbial oxygenases. Photochemical transformations, including photolysis, oxidation, reduction, elimination, hydrolysis, and isomerization, are regarded as the most important abiotic activities affecting organic compounds in experimental and field applications [13]. The interaction of UV energy with organic material in the presence of oxygen is summarized in Figure 1.

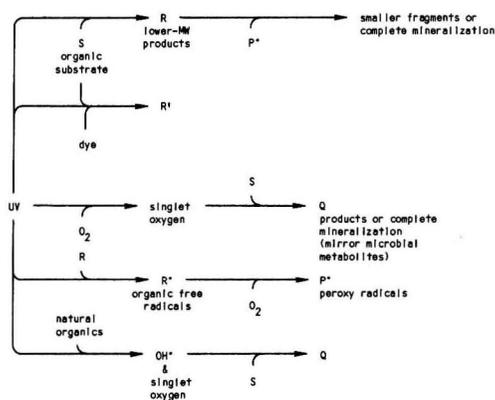


Figure 1. Interactions of UV irradiation with organic material in the presence of oxygen.

## Ozonation

Ozone is a very selective and highly versatile oxidizing agent that has been used extensively in organic chemistry and has been promoted as a method of disinfection for potable water and as a wastewater treatment aid. Details on the specific effects of ozone on different classes of organic compounds can be found in an extensive two-volume review [15, 16]. Unfortunately, most studies on the ozonation of organic substances have been conducted in nonprotic solvents, and these studies often are not directly applicable to the chemical pathways that result from the ozonation of organic compounds in aqueous solutions [17]. The literature must be interpreted and applied judiciously, because solvent effects can be profound. In an aqueous medium, for instance, the oxidative capacity of ozone appears to depend on pH, alkalinity, and the organic and inorganic solute concentrations. For acidic and neutral solutions ( $\text{pH} < 9$ ), ozone reacts predominantly as the parent ozone molecule; these reactions are relatively slow and highly specific depending on the class of organic compound and its bonding structure. Furthermore, it has been reported that oxidation by ozone is almost entirely ineffective in highly acidic aqueous solutions ( $\text{pH} < 2$ ) [18]. In contrast, ozone in basic solutions ( $\text{pH} > 10$ ) is catalytically decomposed by hydroxide ion to a variety of products, including  $\text{OH}^-$  [19, 20] and superoxide anion [16, 21, 22]. At a pH of 10.5, approximately one-half mole of  $\text{OH}^-$  is formed per mole of  $\text{O}_3$  decomposed [19]. Hydroxyl radical is the most potent and effective oxidant known to occur in aqueous solutions [19]. It has an oxidation potential of  $2.8\text{V}(\text{H}^+ = 1.0 \text{ mol/L})$  compared with  $2.07\text{V}$  for ozone in acidic solutions and  $1.36\text{V}$  for chlorine gas [23].

The extreme reactivity of hydroxyl radical leads to rapid oxidation of organic compounds; it reacts with inorganic solutes with little specificity. Although these radicals are quickly consumed (within microseconds), their reactivity makes them critically important to aqueous ozone chemistry [24]. Hydroxyl radicals are vigorously scavenged by carbonate ion and, to a lesser extent, by bicarbonate species. This scavenging shifts the equilibria, and therefore the disproportionation of ozone is accelerated by increased alkalinity [21].

The half-life of ozone depends on the classes of organic solutes that are present in aqueous solutions. Upon ozonation, certain organic compounds form radical-type intermediates that subsequently oxidize other organic substrates and also catalyze the further decomposition of ozone [24]. The presence of iron salts enhances the effect of ozone on organic compounds in domestic wastewater [25]. It has been proposed that ferric ion catalyzes the disproportionation of ozone to its highly reactive decomposition product,  $\text{OH}^-$ . Free ammonia can be oxidized to nitrate by ozone and  $\text{OH}^-$  although ammonia oxidation is a significant factor only when it is present in concentrations equal in magnitude to those of carbonate species and the organic solutes [26]. Radicals, metal salts, and coreacting or scavenging species, therefore, can mediate the effectiveness of oxidation by hydroxyl radical in a complex wastewater matrix. The reactions of ozone in aqueous solution are summarized in Figure 2.

Retort water often contains high ammonia and dissolved inorganic carbon (DIC) concentrations, both of which either react with or scavenge ozone or ozone-disproportionation products. Furthermore, substituted nitrogen heterocycles, a major biorefractory organic chemical class in spent retort water, are not particularly susceptible to attack by ozone [17] (e.g., pyridine reacts extremely slowly and ozone preferentially attacks the carbocyclic ring of quinoline [17]). In contrast,  $\text{OH}^-$  readily undergoes an addition reaction with pyridine to form an hydroxycyclohexadienyl radical [27], which then decomposes at an equally rapid rate [28].

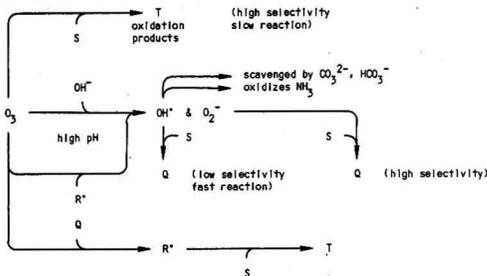


Figure 2. Summary of reactions of ozone with organic compounds in aqueous solution (modified from [21]).

Partial oxidation or cleavage by ozonation of complex high-molecular-weight organic compounds, which are commonly biorefractory, into lower-molecular-weight fragments, can substantially enhance biodegradability. The benefit of partial oxidation has been shown for nonbiodegradable water-soluble polymers [29, 30]. Ozone pretreatment of polyethylene glycol, poly(vinyl alcohol), poly(vinylpyrrolidone), and sodium polyacrylate reduces the molecular weights and improves biooxidation.

#### Combined UV Irradiation/Ozonation

UV radiation catalyzes the disproportionation of ozone into  $\text{OH}^\bullet$  [16, 31, 32] and superoxide ion, and it promotes the production of free organic radicals [33]. In contrast to hydroxide-ion mitigated ozone decomposition, ozone disproportionation by UV radiation is not restricted to the alkaline pH range. Creation of ozone decomposition products at lower pH ranges minimizes carbonate scavenging and ammonia oxidation due to shifts in the ion equilibria; this affords a major advantage to the combined UV/ozonation approach for the mineralization of contaminative solutes. In addition, chemical reactions mediated by UV/ozonation are significantly faster in the acidic than in the basic pH range [34]. Combined UV/ozonation has been reported as superior to the individual treatments for the elimination of biorefractory organic solutes from water and for the treatment of industrial wastewaters [9, 16, 21, 35]. The application of simultaneous UV/ozonation to the mineralization of water supply refractory organic species has been recently reviewed [36].

The destruction of biologically recalcitrant organic solutes by combined UV irradiation/ozonation complements the effects of activated sludge [31]. Used as a pretreatment to biooxidation, it may offer a more economical approach than chemically mediated mineralization of refractory compounds. Structural alterations of solutes effected by brief exposure to UV/ozonation may be sufficient to allow an acclimated microbial community to mineralize a significant portion of the formerly recalcitrant solutes. Preliminary experiments show that some pesticides, munition wastewaters, and industrial wastes can be sufficiently altered by UV/ozonation treatment to make them degradable by acclimated soil microbiota [9, 37]. Perhaps the major drawback to this approach as a pretreatment for biooxidation of oil shale wastewaters is that both ozonation and UV irradiation/ozonation, like UV photolysis, create multiple products from each oxidizable compound [21, 38]. In addition to its role as a complementary treatment step for biooxidation, the chemical alterations effected by UV/ozonation may also model microbial systems in a manner analogous to ozone-decomposition products. The chemical decomposition products from UV irradiation of ozone and the resulting interactions with substrates are summarized in Figure 3.

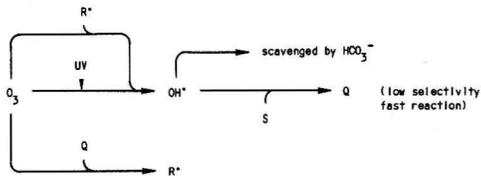


Figure 3. Effects of UV-radiation-mediated ozonation on aqueous organic solutes.

## RESULTS AND DISCUSSION

Ozonation, UV irradiation, and combined UV/ozonation were evaluated both for their ability to directly oxidize organic solutes and for their indirect influence on biodegradability (through minor structural alterations) of refractory compounds in Oxy-6 retort water. Possible mechanisms of organic solute alterations were investigated by determining dissolved organic carbon [39] in time-course samples that had been fractionated by a simple reverse-phase chromatographic method [40].

#### UV Irradiation

Relatively short exposure (120 min) to intense UV radiation was insufficient to mineralize or alter the recalcitrant compounds in raw retort water or in the extracellular fluid from outgrown cultures (spent retort water). The results from subjection of spent Oxy-6 retort water to extensive UV irradiation (300 min) followed by secondary biooxidation are presented in Figure 4. The lower graph is the cumulative UV energy supplied to the photoreactor. Each pair of bars represents a sample withdrawn from the photoreactor at hourly intervals. For each pair, the first bar is the dissolved organic carbon (DOC) concentration after UV irradiation, and the second bar is the DOC concentration after subsequent biological treatment. The black portion of each bar is the DOC concentration of the polar organic solutes (hydrophilic fraction; HpF) and the remaining portion is the concentration of the less-polar solutes (lipophilic fraction; LpF) [40]. Five hours of intensive irradiation did not mineralize a significant amount of DOC (<2%), remove the chromophoric substances that give retort water its characteristic dark brown color, or change the relative polarities of the organic constituents. Furthermore, UV irradiation did not appear to structurally alter the biorefractory organic compounds; biooxidation of irradiated retort water did not mineralize additional carbon compared with nonirradiated, reinoculated control cultures (i.e., the difference in DOC for each pair of bars was equivalent to the control).

Ultraviolet irradiation of retort water may have been ineffective because of the presence of photooxidation inhibitors [20]. Since particulate and colloidal carbonates can protect organic solutes from the effect of UV irradiation [7], the high concentrations of these species in this retort water may have prevented photoalterations. In addition, the chromophoric solutes of the water may have absorbed a significant amount of the UV energy, preventing effective penetration into the water.

#### Ozonation

When low dosages ( $1.5 \times 10^{-6}$  kg/min) of ozone were sparged through raw or spent retort water for short periods (20 to 60 min) the DOC concentration was not substantially reduced nor were the structures of the biorefractory organic solutes altered. The effects of extensive ozonation of spent retort water are presented (Figure 5) in a manner analogous to the results in Figure 4; the lower graph represents the cumulative amount of ozone consumed. Although five hours of ozonation ( $7.1 \times 10^{-6}$  kg/L-min) re-

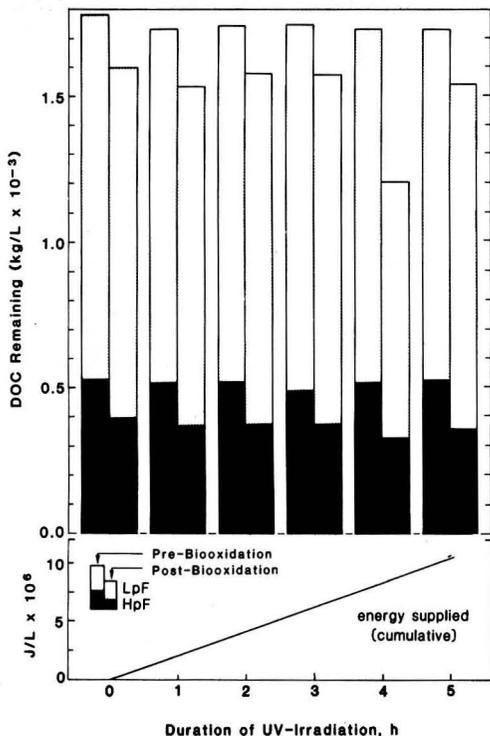


Figure 4. Biooxidation of UV-pretreated spent Oxy-6 retort water.

sulted in total ozone solubilization and consumption of more than  $1.6 \times 10^{-3}$  kg/L, only a small portion of DOC was mineralized (4%). This portion was responsible, however, for the majority of the color of the spent retort water.

In contrast to the low dosages of ozone used in the preliminary experiments, extensive ozonation of spent retort water altered a significant portion of the biorefractory organic solutes; of the DOC that was previously recalcitrant, 14% became amenable to microbial mineralization. Although the enhancement of biological mineralization was almost exclusively at the expense of the more polar compounds (HpF), the concentration of DOC in the HpF after biological oxidation of the five-hour, ozone-treated sample was 16% higher than that of the time-zero, nonozonated, biologically treated sample. These results indicate that a portion of the ozonation products was more highly oxidized, and some of these became biorefractory.

Alteration of the refractory organic compounds and elimination of the chromophoric substances most likely resulted from direct oxidation by the parent ozone molecule; the solution pH probably precluded the decomposition of ozone by OH<sup>-</sup> into its highly reactive radicals. Rather, the susceptible solutes were gradually modified until they were exhausted, at which point ozone was no longer an effective oxidant.

#### Combined UV Irradiation/Ozonation

The organic solutes in raw or spent retort water were resistant to mineralization by short exposures to low dosages of ozone in conjunction with UV radiation. Subsequent biooxidation was not improved by this pretreatment. In contrast, six hours of simultaneous ozonation and UV irradiation of spent retort water mineralized 20% of the organic carbon and appeared to significantly alter the remaining biorefractory compounds. The effects of exten-

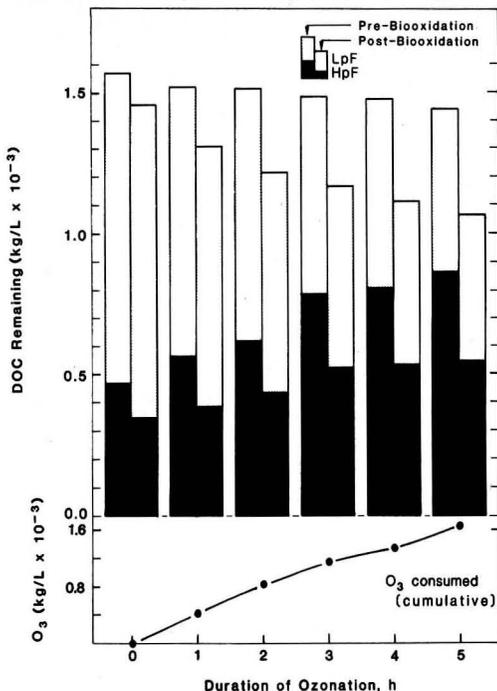


Figure 5. Biooxidation of ozone-pretreated spent Oxy-6 retort water.

sive UV/ozonation of spent retort water are presented in Figure 6; the lower graph represents the cumulative amount of both ozone consumed and UV energy supplied.

Extensive UV/ozone treatment initially either mineralized the LpF organic solutes or transformed them into HpF solutes. After three hours of treatment, the LpF carbon continued to be mineralized, but further conversion to HpF carbon was not observed. The intense color of the spent retort water was almost entirely eliminated, and the usually persistent distinctive odor of the water was reduced to almost undetectable levels.

Three hours of intensive ozonation coupled with UV irradiation also effected considerable structural alteration of the organic solutes in spent retort water, because an acclimated microbial seed was then capable of utilizing approximately  $4 \times 10^{-4}$  kg/L of DOC that was normally unavailable in completely spent retort water. This auxiliary biooxidation was entirely at the expense of newly created HpF organic compounds; biodegradability of retort-water solutes seems to correlate with increasing content of HpF organic carbon. The composition of the water following the serial application of biooxidation, three hours of UV/ozonation, and exhaustive secondary biooxidation was similar to that of the same spent water after five hours of ozonation followed by biooxidation.

Simultaneous UV/ozone treatment of spent water beyond three hours resulted in a reversal of the trend of increasing biodegradability. Additional biodegradable HpF-carbon was not generated, and the HpF that remained appeared to become biorefractory. After six hours of combined UV/ozonation of spent retort water, only 1% of the DOC was susceptible to microbial attack, yet the majority of the solutes that remained were in the HpF. For the six-hour sample, the HpF-carbon actually increased as a result of secondary biotreatment; the bacteria were growing at the expense of the LpF carbon and apparently altering a portion of this carbon to yield refractory HpF compounds. Microbial catabolic incompetence may not

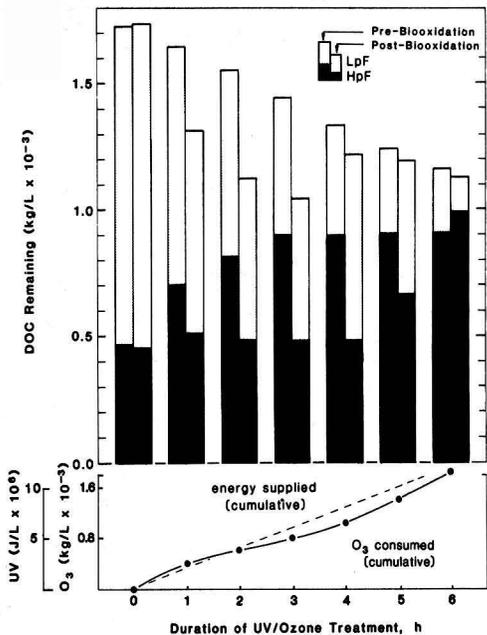


Figure 6. Biooxidation of UV/ozone-pretreated spent Oxy-6 retort water.

have been the only factor limiting the degradation of the remaining solutes; increased toxicity, threshold-concentration effects, or the lack of a specific nutrient or enzyme cofactor may have limited further mineralization of the DOC.

The LpF-fraction from raw, spent, and UV/ozonated spent retort water was analyzed by nitrogen-specific capillary gas/liquid chromatography for volatile nitrogenous organic compounds. Six hours of UV/ozonation eliminated most of the lower- and higher-molecular-weight volatile nitrogen-containing compounds from the LpF (Figure 7). In addition, the concentration of the intermediate-molecular-weight nitrogenous compounds in the LpF was greatly reduced. These compounds had either been mineralized or transformed into HpF nitrogen-bearing compounds.

Gas chromatographic mass spectrometry has revealed that nitrogen heterocycles and aromatic amines accounted for only 25% of the DOC in the six-hour UV/ozonated sample [41]. This would indicate that the biorefractory nature of this sample was not a result of these types of nitrogen-containing compounds alone.

Extensive UV irradiation combined with ozonation effected mineralization of a substantial portion of the DOC after six hours, but further biological treatment was unsuccessful. Although color and odor were nearly eliminated, 41% of the DOC of raw retort water remained after exhaustive serial treatment by primary biooxidation, UV/ozonation, and secondary biooxidation. The organic solutes that remained appeared to be refractory to both chemical and microbial oxidative alteration or mineralization. The dosages of either ozone or UV energy used in this study would be totally uneconomical in any treatment scheme. These data merely emphasize the extreme resistance of the organic solutes in retort waters to mineralization and that biooxidation would probably be of limited utility. A more extensive discussion of the experimental procedure and results has been prepared [42].

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#### LITERATURE CITED

- Jones, B. M., R. H. Sakaji, and C. G. Daughton, "Treatment of Wastewater from Modified In-Situ Oil Shale Retorting," in *Energy and Environment Division 1980 Annual Report*, Lawrence Berkeley Laboratory report (LBL-11989), 1981.
- Jones, B. M., R. H. Sakaji, J. F. Thomas, and C. G. Daughton, "Microbial Aspects of Oil Shale Wastewater Treatment," in *Energy and Environment Division 1981 Annual Report*, Lawrence Berkeley Laboratory report (LBL-13500), 1982.
- Daughton, C. G., R. H. Sakaji, and B. M. Jones, unpublished data, LBL-SEEHRL Oil Shale Waste Treatment Program, 1982.
- Raphaelian, L. A. and W. Harrison, "Organic Constituents in Process Water from the In-Situ Retorting of Oil from Oil-Shale Kerogen," Argonne National Laboratory report (ANL/PAG-5), 1981.
- Jerina, D. M., "Hydroxylation of Aromatics: Chemical Models for the Biological Processes," *CHEMTECH* 3, 120 (1973).
- Crosby, D. G., "Environmental Photooxidation of Pesticides," in *Proceedings of the Conference on the Degradation of Synthetic Molecules in the Biosphere: Natural, Pesticidal, and Various Other Man-Made Compounds*, San Francisco, Calif., June 12-13, 1971; National Academy of Sciences: Washington, D.C., 1972.
- Manny, B. A., M. C. Miller, and R. G. Wetzel, "Ultraviolet Combustion of Dissolved Organic Nitrogen Compounds in Lake Waters," *Limnol. Oceanog.* 16, 71 (1971).
- Plimmer, J. R., "Principles of Photodecomposition of Pesticides," in *Proceedings of the Conference on the Degradation of Synthetic Molecules in the Biosphere: Natural, Pesticidal, and Various Other Man-Made Compounds*, San Francisco, Calif., June 12-13, 1971; National Academy of Sciences, Washington, D.C., 1972.
- Kearney, P. C., Q. Zeng, and J. M. Ruth, "Oxidative Pretreatment Accelerates TNT Metabolism in Soils," *Chemosphere* 12, 1583 (1983).
- Mill, B. A., D. C. Hendry, and H. Richardson, "Free-Radical Oxidant in Natural Waters," *Science* 207, 886 (1980).
- Jones, P. H., D. Prasad, M. Heskins, M. H. Morgan, and J. E. Guillet, "Biodegradability of Photodegraded Polymers I. Development of Experimental Procedures," *Environ. Sci. Technol.* 8, 919 (1974).
- Anonymous, "UV Light, Bacteria Destroy Toxic Wastes," *Chem. Eng. News*, 35, April 20, 1981.
- Bull, A. T., "Biodegradation: Some Attitudes and Strategies of Microorganisms and Microbiologists," in "Contemporary Microbial Ecology," D. C. Elwood, et al. (Eds.), Academic Press: New York, N.Y. (1980).
- Foote, C. S., "Photosensitized Oxygenations and the Role of Singlet Oxygen," *Acc. Chem. Res.* 1, 104 (1968).
- Bailey, P. S., "Ozonation in Organic Chemistry: Olefinic Compounds," Academic Press, New York, NY (1978), Vol. I.
- Bailey, P. S., "Ozonation in Organic Chemistry: Nonolefinic Compounds," Academic Press, New York, N.Y. (1982), Vol. II.
- Bailey, P. S., "Organic Groupings Reactive toward Ozone Mechanisms in Aqueous Media," in "Ozone in Water and Wastewater Treatment," F. L. Evans, (Ed.); Ann Arbor Science Pub., Inc., Ann Arbor, Mich. (1972).
- Suzuki, J., "Study on Ozone Treatment of Water-Soluble Polymers. I. Ozone Degradation of Polyethylene Glycol in Water," *J. Appl. Polym. Sci.* 20, 93 (1976).
- Hoigné, J. and H. Bader, "Ozone and Hydroxyl Radical-Initiated Oxidations of Organic and Organometallic Trace Impurities in Water," *ACS Symp. Ser.* 82, 292 (1978).
- Larson, R. A., "Environmental Chemistry of Reactive Oxygen Species," *CRC Crit. Rev. Environ. Cont.* 8, 197 (1978).
- Hoigné, J. and H. Bader, "The Role of Hydroxyl Radical Reactions in Ozonation Processes in Aqueous Solutions," *Water Res.* 10, 377 (1976).
- Weber, W. J., Jr., "Physicochemical Processes for Water Quality Control," Wiley-Interscience, New York, N.Y. (1972).
- Peleg, M., "Review Paper: The Chemistry of Ozone in the Treatment of Water," *Water Res.* 10, 361 (1976).
- Hoigné, J. and H. Bader, "Ozonation of Water: Selectivity and Rate of Oxidation of Solutes," *Ozone: Sci. Eng.* (Pergamon Press, Ltd.) 1, 73 (1979).

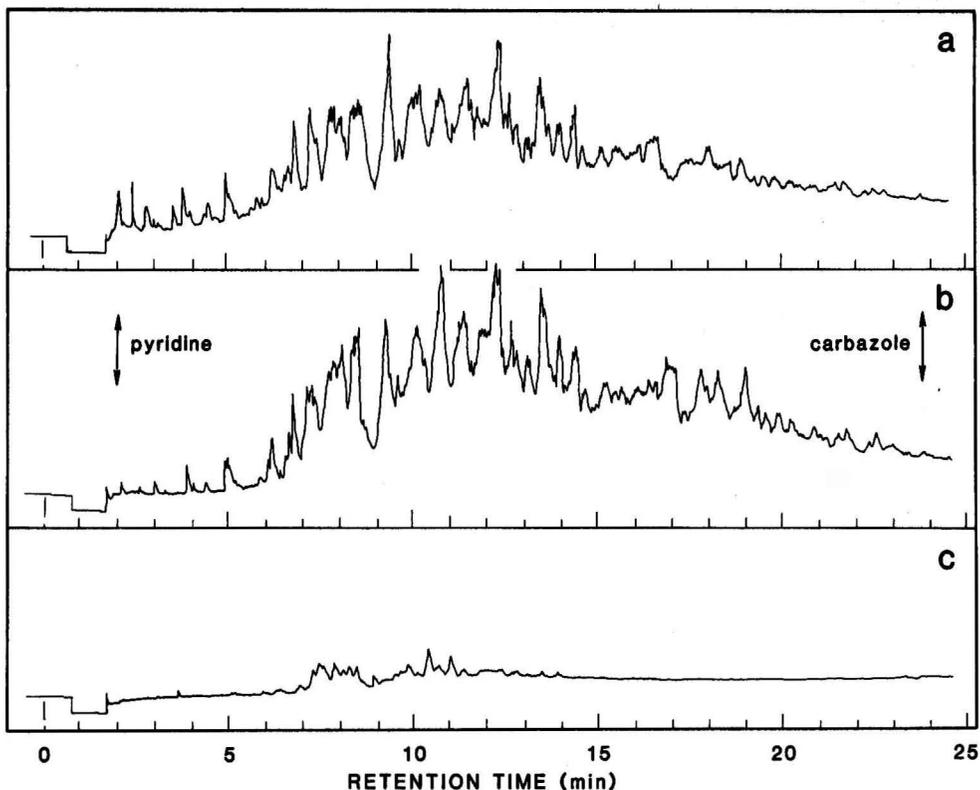


Figure 7. Gas chromatograms of raw, spent, and UV/ozone-treated spent Oxy-6 retort water (nitrogen-selective detection).

25. Shapiro, R. H., K. J. Kolonko, R. T. Binder, R. M. Barkley, G. A. Eiceman, L. P. Haack, and R. E. Sievers, "Detection and Identification of Organics in Domestic Wastewater Before and After Ozonation," in *Proceedings of the 4th Joint Conference on Sensing of Environmental Pollutants*, American Chemical Society, New Orleans, LA, 1978.
26. Hoigné, J., and H. Bader, "Ozonation of Water: Kinetics of Oxidation of Ammonia by Ozone and Hydroxyl Radicals," *Environ. Sci. Technol.* **12**, 79 (1978).
27. Dorman, L. M. and C. E. Adams, "Reactivity of the Hydroxyl Radical in Aqueous Solutions," U.S. Dept. Commerce (NSRDS-NBS 46), 1973.
28. Cercek, B. and M. Ebert, "Pulse Radiolysis Studies of the Reaction of H and OH radicals and Hydrated Electrons with Pyridine," *Trans. Faraday Soc.* **63**, 1687 (1967).
29. Suzuki, J., H. Nakagawa, and H. Ito, "Study on Ozone Treatment of Water-Soluble Polymers, II. Utilization of Ozonized Polyethylene Glycol by Bacteria," *J. Appl. Polym. Sci.* **20**, 2791 (1976).
30. Suzuki, J., K. Hukushima, and S. Suzuki, "Effect of Ozone Treatment upon Biodegradability of Water-Soluble Polymers," *Environ. Sci. Technol.* **12**, 1180 (1978).
31. Prengle, H. W., Jr. and C. E. Mauk, "New Technology: Ozone/UV Chemical Oxidation Wastewater Process for Metal Complexes, Organic Species and Disinfection," *AIChE Symp. Ser. Series No. 178*, **74**, 228 (1978).
32. Sierka, R. A. and W. F. Cowen, "The Catalytic Ozone Oxidation of Aqueous Solutions of Hydrazine, Monomethyl Hydrazine and Unsymmetrical Dimethylhydrazine," in *Proceedings of the 35th Industrial Waste Conference*, Ann Arbor Science Pub., Inc., Ann Arbor, Mich. 1980, 406.
33. Prengle, H. W., Jr., C. E. Mauk, R. W. Legan, and C. G. Hewes III, "Ozone/UV Process Effective Wastewater Treatment" *Hydrocarbon Process.* **54**, 82 (1975).
34. Peyton, G. R., F. Y. Huang, J. L. Bursleson, and W. H. Glaze, "Destruction of Pollutants in Water with Ozone in Combination with Ultraviolet Radiation. I. General Principles and Oxidation of Tetrachloroethylene," *Environ. Sci. Technol.* **16**, 448 (1982).
35. Kuo, P. P. K., E. S. K. Chian, and B. J. Chang, "Identification of End Products Resulting from Ozonation and Chlorination of Organic Compounds Commonly Found in Water," *Environ. Sci. Technol.* **11**, 1177 (1977).
36. Glaze, W. H., G. R. Peyton, F. Y. Huang, J. L. Bursleson, and P. C. Jones, "Oxidation of Water Supply Refractory Species by Ozone with Ultraviolet Radiation," 1980, EPA-600/2-80-110.
37. Kearney, P. C., J. R. Plimmer, and Z.-M. Li, "UV-Ozonation and Land Disposal of Aqueous Pesticide Wastes," in *Fifth International Congress of Pesticide Chemistry Proceedings*, Pergamon Press, Oxford, England, (1982).
38. Kolonko, K. J., R. H. Shapiro, R. M. Barkley, and R. E. Sievers, "Ozonation of Caffeine in Aqueous Solution," *J. Org. Chem.* **44**, 3769 (1979).
39. Langlois, G. W., B. M. Jones, R. H. Sakaji, and C. G. Daughton, "Quantitation of Carbon in Oil Shale Process Wastewaters: Coulometry Coupled with UV-Peroxydisulfate and High-Temperature Oxidation," *ASTM J. Test. Eval.* **12**(4), 227 (1984).
40. Daughton, C. G., B. M. Jones, and R. H. Sakaji, "Rapid Fractionation of Aqueous Samples by Reverse-Phase Partitioning," in "A Manual of Analytical Methods for Wastewaters," 2nd ed.; C. G. Daughton, (Ed.); Lawrence Berkeley Laboratory report (LBL-17421), Chapter I, 1984.
41. Condit, M. K., "Characterization and Treatment of Organic Compounds and Trace Elements in Oil Shale Wastewaters," Ph.D. Thesis, University of Colorado, 1984.
42. Jones, B. M., G. W. Langlois, R. H. Sakaji, and C. G. Daughton, "Ozonation and UV Irradiation: Effect on Oil Shale Biorefractory Organic Solutes," LBL-SEEHRL Oil Shale Waste Treatment Program, Lawrence Berkeley Laboratory report (LBID-549), 1982.



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# A Mathematical Model of Settling Velocity Enhancement by Kinetic Control

## Advances in the technique of the removal of metal ions from solution by precipitation with hydroxide ion.

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The process of removal of metal ions from solution by precipitation with hydroxide ion has been a commercially viable technique for many years. Fundamental to the process is the formation of the hydroxide precipitate of the metal, followed by agglomeration or flocculation into larger clumps, which then settle into a colloidal sludge as the remaining liquid overflows from the top of the separator. The sludge is withdrawn from the bottom of the separator and disposed of in a landfill or by other means.

Standard upflow clarifiers have been used for the separation process. However, this study focused on reactor-clarifiers where the addition of chemicals and thus the precipitation of solids takes place within the same vessel. This type of separator is important because the Environmental Protection Agency has designated the reactor-clarifier as a recommended process for the metal finishing industry [1].

Accepted design procedures for clarifiers have been based on empirical techniques which employ settling velocity studies [2]. The objective of this work is to derive and verify a time-dependent clarifier model based on kinetics and solid-fluid mechanics principles which can be readily programmed for digital computation, and which employs settling velocity studies for input information. The first studies were conducted with  $\text{Fe}(\text{OH})_3$  flocs precipitated from ferric sulfate solutions. These solutions were of interest because they simulate rinse waters from steel pickling operations. The model proved successful in describing the ferric hydroxide removal process; therefore, it was decided to broaden the area of study to include other metal ions to further prove the model applicable in describing the process. The second series of tests which are reported in this paper employed aluminum sulfate solutions which simulate wastes from the aluminum etching industry. Furthermore, the aluminum ion provides us with a lighter weight atom and most certainly with a different hydroxide complex and a floc density different from that of ferric hydroxide, and therefore provides another aspect in the testing of the model.

The original studies by Graves [3] showed that freshly precipitated, relatively undisturbed ferric hydroxide flocs formed large and fragile aggregates which settled several times faster than extensively stirred floc. She also noted that flocs, once disrupted by stirring, did not reaggregate. Thus it appears that van der Waals type forces are not responsible for holding these large flocs together and that floc disruption is irreversible.

The model as developed by Graves was applicable to the production of ferric hydroxide floc in upflow clarifiers. This floc is well-stirred because of the manner in which the upflow clarifiers operate. Two parameters

were determined by Graves from liter cylinder tests. These are the effective radius  $r$  and  $\alpha$ , a parameter relating to the slurry viscosity. Strang [4], using paddle type stirrers and a specially constructed bench scale apparatus to measuring settling velocity, was able to correlate  $r$  and  $\alpha$  with the rapid mix chamber mean residence time  $t$ . Strang then was able to extend the model to describe the operation of reactor-clarifiers.

### MATHEMATICAL MODEL AND TECHNIQUE OF VERIFICATION

The original model proposed for orthokinetic flocculation included:

1. a catchup mechanism associated with different terminal velocities of particles of different size;
2. a mechanism based on the turbulent eddies generated in the liquid by the dissipation of energy by the settling particles;
3. a dependence of the floc particle density on size of the floc.

It was assumed that composite particles aggregate from unit elementary particles or smaller composite particles under the influence of the catchup and turbulent mechanism and disrupt under the influence of gravity, viscous drag, and bulk flow of the liquid. A complete explication of the model is given in the article by Graves, Schnelle, and Wilson [5].

During the testing of the model, it was discovered that the effect of the parameters of the kinetic mechanism was minimal when comparing predicted and experimental results. Thus the model was simplified to a lumped parameter material balance. A variable cross sectional area is allowed for by the model, making it applicable both to standard upflow-clarifiers and reactor-clarifiers. The following simplified formula for the slurry viscosity was adopted as well:

$$\mu = \mu_0 \exp(\alpha c) \quad (1)$$

Results of testing this model for the standard upflow-clarifier are reported by Wilson, Graves, and Schnelle [6].

Strang [4] was able to quantify the mixing time effect on floc formation and to formulate a model and verification procedure for a reactor-clarifier. Results of this study are reported by Strang, Schnelle, and Wilson [7]. The model verification technique is summarized in Figure 1. Operation should be conducted at the optimum pH for precipitation. It is also convenient to determine the amount of precipitant required to bring the metal-bearing solution to the optimum pH for metal removal. Sludge concentrations can be quantified by determination of the total suspended solids or from the settleable solids volume fraction (SSVF), a



sulfate was prepared. The synthetic wastewater was stored in Nalgene containers and diluted to the desired concentration. Aluminum concentration was determined by a Perkin-Elmer model 403 atomic absorption spectrophotometer with a nitrous oxide-acetylene flame at standard operating conditions.

**Settleable Solids Volume Fraction (SSVF)**

In all of the work it has been found that settleable solids volume fraction is a useful and directly relevant measure of concentration. Moreover, SSVF is more readily correlatable with the results of mathematical modeling. To determine SSVF, 100-ml samples of suspension are allowed to settle for a 24-hour period in a graduated cylinder. During the long time period most of the inter-particle water will escape the settled solids. The SSVF was taken as the volume of the remaining suspended solids divided by the original volume of the suspension.

**Optimum pH for Removal of Aluminum from Solution**

Optimum pH was determined to be about 5.4 by standard methods for wastewater analysis. Aluminum concentration was found to be less than 2.0 mg/liter at this pH. Since literature values of pH = 5.5 were reported [8] as optimum, it was decided to use 5.5 as the optimum pH at which to operate both the bench scale and the pilot scale apparatus.

It was also found to be convenient to prepare a curve of amount of NaOH required to bring aluminum sulfate solutions to optimum pH. This relationship was found to be linear.

**Aluminum Ion Concentration Effect on SSVF**

During the course of the experiments it was found that controlled laboratory experiments in which the measured aluminum ion concentration and SSVF were more accurately known were the most reliable information to use to

TABLE 1. FLOC DENSITY AS A FUNCTION OF ALUMINUM ION CONCENTRATION AND SSVF

Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 18H <sub>2</sub> O (mg/liter)	Al ion (mg/liter)	SSVF	Floc Density (g/cm <sup>3</sup> )
500	40.5	0.100	1.00696
1000	81.0	0.145	1.00946
1500	121.5	0.178	1.00115
2000	162.0	0.207	1.00133
2500	202.5	0.232	1.00148
3000	243.0	0.254	1.00162
4000	324.0	0.295	1.00186

determine the SSVF for modeling. Therefore, a relationship between aluminum ion concentration and SSVF was established; then, aluminum concentrations from the solution in the operating equipment, as determined by the atomic absorption spectrophotometer, were used to calculate the SSVF for use in the mathematical model. The SSVF and aluminum ion concentration have been statistically fit to a power law of the form of Equation 5, where Al = aluminum concentration in mg/liter; and  $a = 0.0154$ ,  $b = 0.511$ , with a correlation coefficient of 0.995. Data from the bench scale apparatus to be discussed in the next section also generally agreed with the beaker studies and confirmed the difficulty in determining SSVF from operation equipment.

**Estimate of Floc Density**

Measurements of SSVF were used to estimate floc density, a parameter needed in the model. The floc was assumed to consist of Al(OH)<sub>3</sub> with a density of 2.42 g/cm<sup>3</sup>. The calculation of floc density is made on the basis of 100 cm<sup>3</sup> of sample. The floc mass in 100 cm<sup>3</sup> is determined as the sum of the mass of Al(OH)<sub>3</sub> and the mass of the water. Table 1 presents the SSVF, determined for the solution concentrations used in this work, along with the floc density. This calculated density was used in determining r and

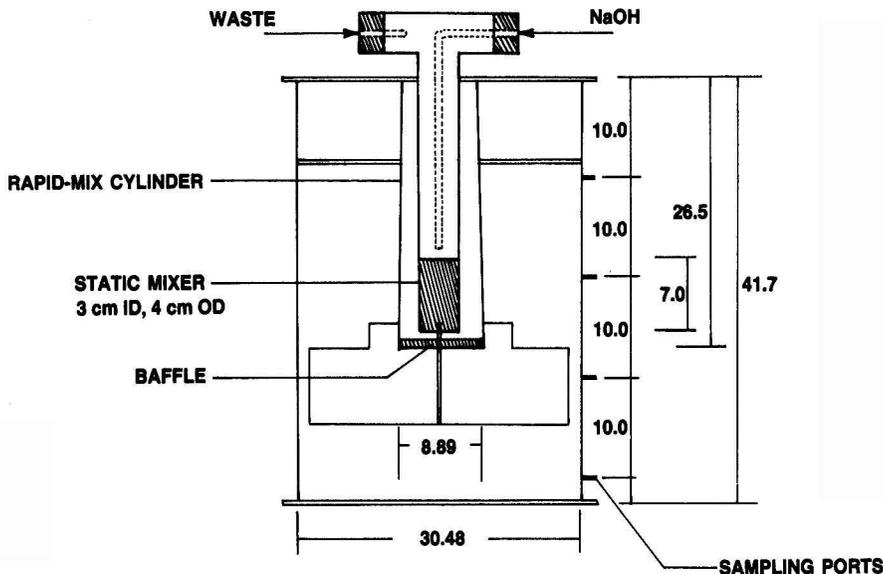


Figure 2. Bench scale apparatus.

$\alpha$ , as will be reported in the next section, with the realization that the true density of settling floc would differ from the value calculated. However, as yet a better method for determining the true density has not been found. This method has the advantage of not being arbitrary, giving reproducible results, and producing a reasonable correlation of the data by the mathematical model.

## BENCH SCALE APPARATUS STUDIES

### Experimental Apparatus

In the original experiments by Graves [3] and Strang [4], mixing was carried out by stirrers with paddle blades. In order to reduce the retention time for mixing, in this study a Koch Engineering Co., of Wichita, Kansas, PVC two element static mixer was used. The static mixer is 3 cm in diameter and 7 cm long. The mixer was placed in a PVC pipe and held in place by a ring at the bottom of the pipe. Mixer mean residence time was determined by dividing the free volume of fluid surrounding the mixer by the flow rate of fluid through the mixer.

The free volume was determined by measuring the volume of water displaced when the static mixer was immersed in a vessel containing a known volume of water. The free volume is the difference between the original volume and the volume displaced and was found to be 43.9 cm<sup>3</sup>.

The bench scale apparatus is illustrated in Figure 2 and was constructed mainly of Plexiglas. The outer body is 41.7 cm long and 30.48 cm in diameter. The inner cylinder contains the static mixer and is 26.5 cm long and 8.89 cm in diameter. Four sample ports are located at 10-cm intervals along the side of the outer body. Wastewater is delivered to one side of the run of a tee where it makes the 90° turn onto the mixer. The 0.50 N NaOH solution is fed from the other side of the run of the tee through a glass tube with a

90° bend. The NaOH solution exits the glass tube on the top of the static mixer, where it encounters the wastewater. Mixing, chemical reaction, and precipitation begin all at once at the top of the static mixer. The precipitated  $Al(OH)_3$  then flows through a baffle into the main body of the apparatus to flocculate and form a sludge blanket where the solid-liquid separation takes place. The clarified liquid flows up and out over a weir positioned at the top of the unit. The total volume of the apparatus is about 23 liters.

### Results

Prior to each run the apparatus was filled with tap water, so that steady-state operation would be approached quickly without having to take into account the solids precipitated while the unit was being filled. Wastewater flow rate was adjusted to give the desired mixer mean residence time, and the NaOH solution flow rate was adjusted to give the optimum pH. The sludge blanket was allowed to reach a height of at least 22 cm. Then, two 100-ml samples were taken from the top of the sludge blanket to determine SSVF. Flows were then shut off. The settling velocity of the blanket was determined by recording the blanket height *versus* time and fitting a straight line to the linear portion of the curve. The slope of the straight line is therefore the zone settling velocity of the suspension. This technique is the same as was developed by Strang [7].

The settling velocity data are segregated by mean residence time,  $t$ , and plotted versus SSVF. Figure 3 is a typical plot for a mean residence time of 0.69 seconds. Aluminum sulfate concentrations used in these runs are listed in Table 1. Data for infinite mixing time were obtained from experiments in liter beakers.

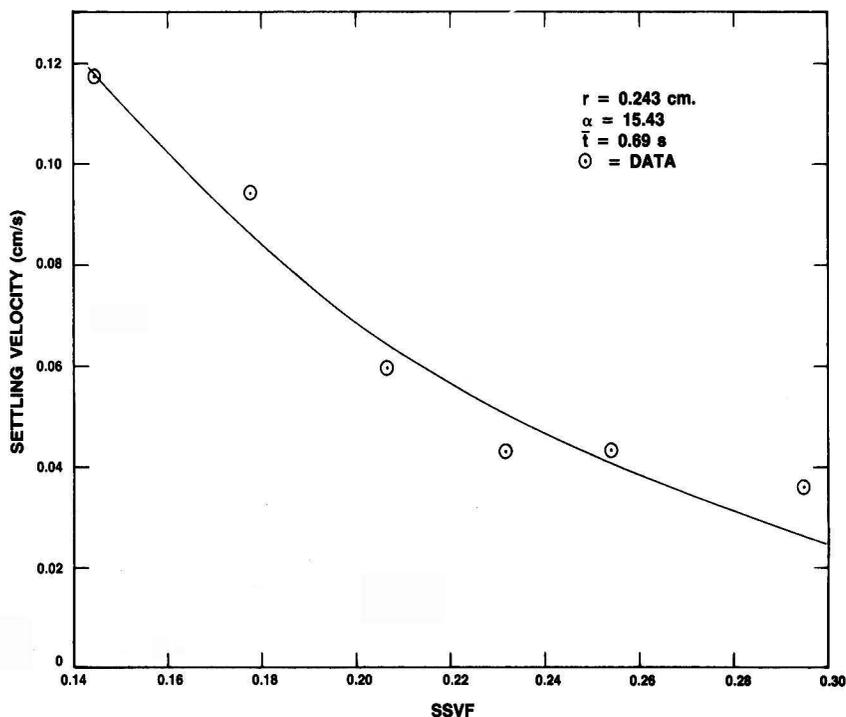


Figure 3. Data and model predictions of settling velocity versus SSVF,  $t = 0.69$  sec.

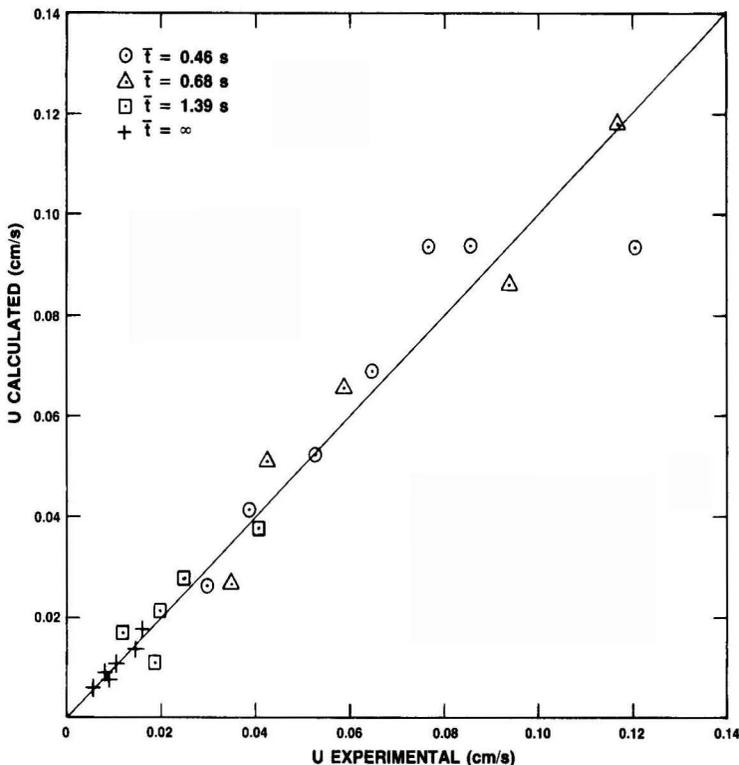


Figure 4. Experimental versus calculated settling velocities for the bench scale apparatus.

Equation 2 is now fit to these data using an iterative technique which employs a minimization of the sum of the squares of the differences between the calculated settling velocity,  $u$  and the measured value of  $u$ . Figure 4 presents a summary of the data analysis exhibiting experimental values of settling velocity versus calculated values. These results verify the use of Equation 2 in this part of the modeling study. Using the values of  $r$  and  $\alpha$  reported in Table 2, which had been calculated from the statistical analyses, curves such as shown in Figure 3 were calculated. A comparison of these curves with the data confirms Equation 2 as an appropriate model for predicting the settling velocity from the SSVF. Using these curves for any given SSVF, it can be observed that the settling velocity decreases as the mixer mean residence time increases.

Two empirical equations were developed to describe the variation of  $r$  and  $\alpha$  with mixer mean residence time  $\bar{t}$ .

$$r = r^* e^{-K_1 \bar{t}} + r_\infty \quad (6)$$

$$\alpha = \alpha^* e^{-K_2 \bar{t}} + \alpha_\infty \quad (7)$$

where in this case the values of the constants are as follows:

$$\begin{array}{ll} r^* = 0.307 \text{ cm} & \alpha^* = 4.69 \\ r = 0.065 \text{ cm} & \alpha = 11.37 \\ k_1 = 0.873 \text{ s}^{-1} & k_2 = 0.114 \text{ s}^{-1} \\ \text{correlation coefficient} = 0.993 & \text{correlation coefficient} = 0.749 \end{array}$$

In both equations, as the mean residence time approaches infinity, the argument of the exponential approaches zero. The values of  $r$  and  $\alpha$  then approach the values generated during infinite mixing time. Thus, as  $\bar{t} \rightarrow \infty$ ,  $r \rightarrow 0.065$  and

$\alpha \rightarrow 11.37$ . The experimental values determined for  $r$  and  $\alpha$  are listed in Table 2 and compared with the values calculated from Equations 6 and 7. It should be noted that Equations 6 and 7, which are a good fit to the data of this work differ from Equations 3 and 4 which were developed by Strang in his study [7].

## PILOT SCALE STUDIES

### Experimental Apparatus

The pilot scale reactor-clarifier system was constructed by Graves [9] and Schroeder [10] and is shown in Figures 5 and 6. The static mixer and mixer housing were the same as those used in the bench scale studies. The pilot scale reactor-clarifier was constructed from a Plexiglas cylinder 122 cm high and 45.7 cm in outer diameter, and a sheet metal cone 13.98 cm in diameter at the top, 25.4 cm in diameter at the bottom, and 87 cm high. The mixer tee was inserted into the top of the cone for use of the apparatus with the static mixer.

TABLE 2. EXPERIMENTAL AND CALCULATED VALUES OF  $r$  AND  $\alpha$

$\bar{t}$ (s)	$1/\bar{t}$ (s <sup>-1</sup> )	Measured values		Calculated values	
		$r$ (cm)	$\alpha$	$r$ (cm)	$\alpha$
$\infty$	0	0.065	11.32	0.065	11.32
1.39	0.719	0.155	15.38	0.156	15.32
0.69	1.45	0.243	15.43	0.233	15.66
0.46	2.17	0.262	15.96	0.271	15.77

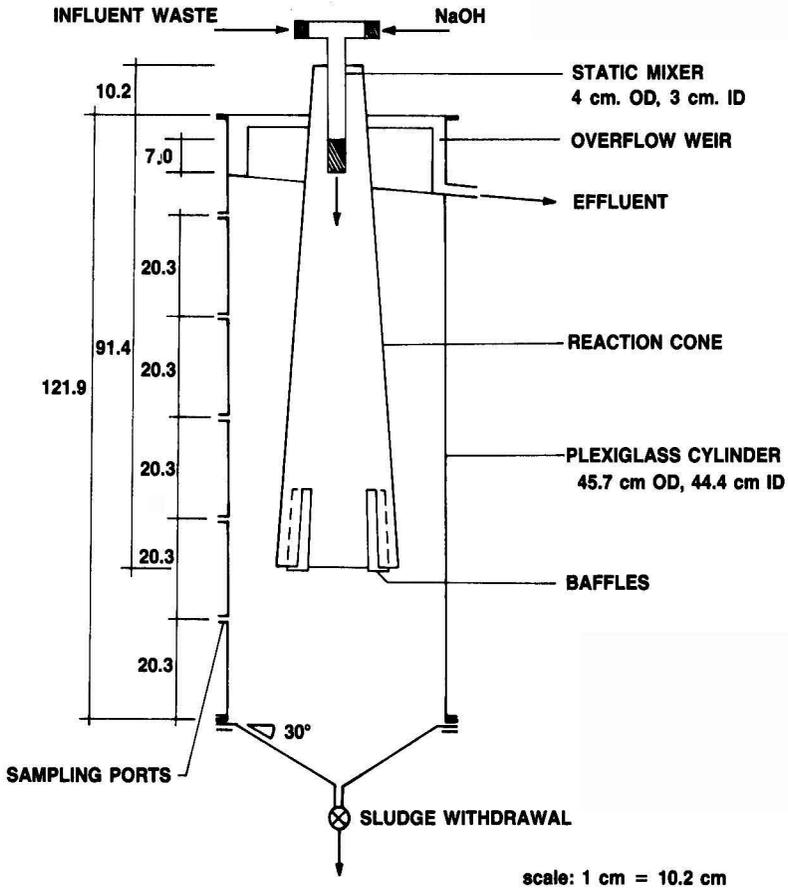


Figure 5. Pilot scale reactor-clarifier.

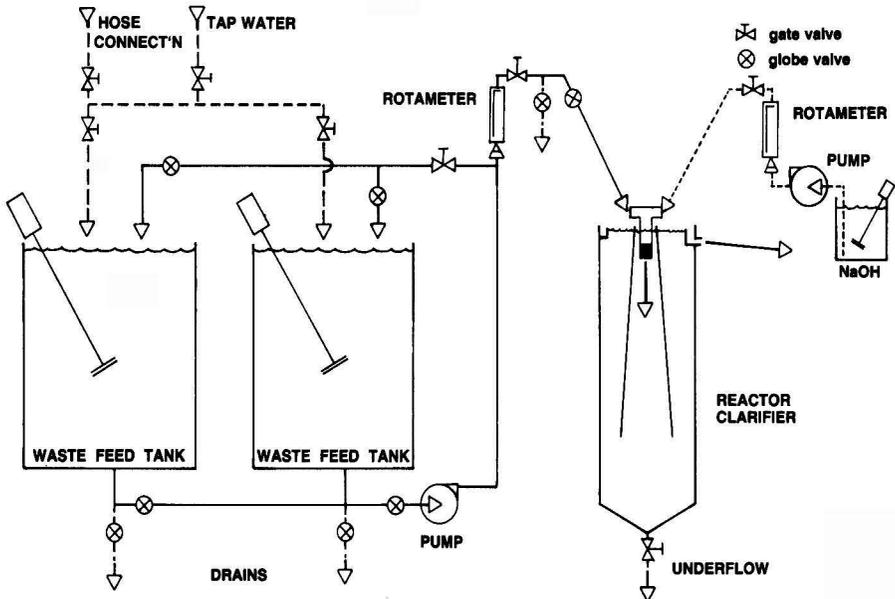


Figure 6. Schematic of reactor-clarifier flow system.

The method chosen for testing the mathematical model was to overload the clarifier system and measure the rate of rise of the sludge blanket in the clarifier. Then, the blanket rise velocity can be compared to that predicted by the model.

The operation of the pilot scale reactor-clarifier is similar to that of the bench scale apparatus. The simulated wastewater and 0.50 N NaOH are fed to the mixer tee at the top of the clarifier cone where precipitation begins. The precipitate then flows down through the cone through baffles at the bottom of the cone and into the main body of the apparatus where it continues to flocculate and begins to separate from the accompanying liquid. Sludge was not wasted from the bottom of the clarifier during the run.

A typical experimental run was begun by filling the apparatus with tap water and determining the desired flowrates of wastewater and NaOH. Then, flows were initiated and a timer was started. After the sludge blanket had risen above the level of the feed plane, the blanket height was recorded as a function of time.

#### Modeling Considerations

The lumped-parameter upflow clarifier model developed previously [5] is combined with Equations 6 and 7 to produce a model for clarifier operation. The model was used to predict the sludge blanket height as a function of time in the region above the feed plane, which is located at 40.5 cm above the bottom of the Plexiglas cylinder. Figure 7 is a typical plot illustrating the blanket height versus time data. The model prediction appears to be good for an increment of about 15 cm above the feed plane. These data can then be linearly regressed to obtain the sludge blanket rise velocity, which is defined as the slope of the line obtained during the regression. The model requires the in-

put of a number of parameters which are listed in Table 3 for this work.

#### Results

Four series of runs were made with the pilot scale apparatus, each at different concentrations of aluminum ion. For each concentration three flowrates and thus three mixer mean residence times were used. Table 4 presents a summary of the experimental data including influent aluminum and aluminum sulfate concentrations, influent SSVF, influent flow rate, mixer mean residence times,  $r$  and  $\alpha$  parameters, experimental blanket rise velocity, and model predicted blanket rise velocity. Typical data for blanket height as a function of time are plotted in Figure 8 for an influent aluminum concentration of 243 mg/liter. As can be seen from Table 4, model predictions for the various influent concentrations are in good agreement with the experimental values. Blanket rise velocity versus flow rates determined from Figure 8 are plotted in Figure 9 for the same aluminum concentration. Comparing these data with those for  $\text{Fe}(\text{OH})_3$  taken by Strang [7] shows the same trends. The model gives a good fit to both sets of data, and in both cases the rate of increase of blanket rise velocity with flow rate increases with increasing metal ion concentration.

#### DISCUSSION

This study has confirmed that the mathematical model which was successfully applied to ferric hydroxide floc in earlier studies can also be applied to aluminum hydroxide floc produced in reactor-clarifiers. The increase of floc settling velocity with decreasing mixer mean residence time has also been confirmed for aluminum hydroxide floc. Strang noted [7] that the variation of reaction rate to

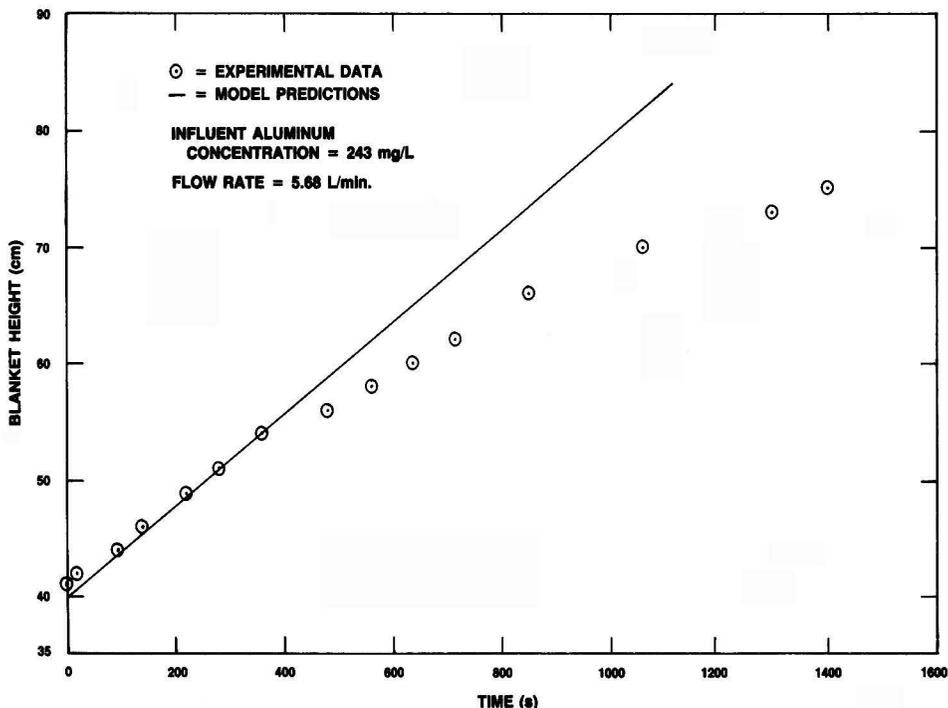


Figure 7. Blanket height versus time, typical data from pilot scale apparatus.

TABLE 3. MODEL PARAMETERS FOR PILOT SCALE REACTOR-CLARIFIER

Parameter	Value Used
Clarifier Geometry	
Radius of casing	22.6 cm
Upper radius of cone	6.99 cm
Lower radius of cone	12.7 cm
Height of clarifier	121.9 cm
Height of feed plane	40.5 cm
Numerical Procedure Constants	
Integration time increment	0.5 to 2.0 min (Note 1)
Number of axial increments	30
Total operation time	as selected by programmer (Note 2)
Flow Rates	
Sludge wasting rate	0.0 ml/s
Influent flow rate	experimental value in ml/s
Physical Properties	
Effective particle radius	(Note 3)
Slurry viscosity parameter	(Note 3)
Influent SSVF	SSVF = $a \cdot Al^b$ (Note 4)
Density of water	1.0 g/cm <sup>3</sup>
Density of floc	(Note 5)

NOTES:

1. Depending on number of data points desired.
2. Total operating time is adjusted during computer runs to acquire enough significant output data for analysis. Several runs may be required to get desired data.
3. See Table 2, measured values used.
4. Al = aluminum concentration in mg/liter  
 $a = 0.0154$      $b = 0.511$

form the hydroxide should result in different parameters for the equations representing  $r$  and  $\alpha$  as functions of the mixer mean residence time  $\bar{t}$ . This work produced a noticeably different set of parametric equations for  $r$  and  $\alpha$ . However, these equations were good representations of the data.

Strang [7] reported that velocity gradients in the rapid mixer were always sufficiently large to disrupt the floc instantaneously. It has also been found in these studies that well mixed floc fails to re-agglomerate, indicating that agglomeration and disruption of these flocs are not readily reversible. Moreover, agglomeration appears to occur most readily within less than a minute after the solutions are mixed. These facts suggest that agglomeration of the

hydroxide flocs is brought about by the continued precipitation of filaments, meshes, and other forms of the hydroxide from the remaining supersaturated solution after it has moved from the rapid mixer into areas of the clarifier where the velocity gradients are small enough not to tear the aggregates to pieces. This in turn suggests that the performance of reactor-clarifiers would be markedly improved by employing a mixer that would produce the most complete mixing in as short a time as possible. The in-line static mixer used in the study was chosen because it has these desired characteristics. Furthermore, there are no moving shafts as in a paddle mixer, and thus velocity gradients will be as low as possible, helping to discourage floc disruption. Continuing efforts to investigate other metal hydroxides and application of the model to industrial size reactor-clarifiers are most certainly warranted.

Acknowledgement

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NOMENCLATURE

- $A(x)$  = cross sectional area of clarifier at a height  $x$  above the bottom (cm<sup>2</sup>)
- Al = aluminum ion concentration (mg/liter)
- $a$  = constant in Equation 5 (units to agree with Al)
- $b$  = constant in Equation 5 (unitless)
- $c$  = SSVF
- $c_n$  = number density of  $n$ -particles at  $(x, t)$
- $c(x, t)$  =  $c_1, c_2, \dots, c_N$
- $D_n$  = effective axial diffusion constant of an  $n$ -particle at  $(x, t)$  (cm<sup>2</sup>/s)
- $F_n$  = flocculation and disruption rates for  $n$ -particles per unit volume (cm<sup>-3</sup> s<sup>-1</sup>)
- $g$  = gravitational constant (980 cm/s<sup>2</sup>)
- $K_1$  = constant in Equation 3 (s)
- $K_2$  = constant in Equation 4 (s)
- $k_1$  = constant in Equation 6 (s)<sup>-1</sup>
- $k_2$  = constant in Equation 7 (s)<sup>-1</sup>
- $N$  = number of elementary particles in the largest composite particle permitted
- $r$  = effective particle radius (cm)
- $r^*$  = constant in Equation 6 (cm)
- $r_\infty$  = constant in equation 6 (cm)
- SSVF = Settleable Solids Volume Fraction
- $t$  = time (s)
- $\bar{t}$  = mean residence time (s)
- $u$  = settling velocity (cm/s)

TABLE 4. EXPERIMENTAL RESULTS AND MODEL PREDICTIONS FOR PILOT SCALE REACTOR-CLARIFIER

Aluminum Sulfate (mg/liter)	Aluminum (mg/liter)	Influent Flow Rate (liter/min)	Mixer Mean Residence Time(s)	$r$ (cm)	$\alpha$	Blanket Rise Velocity (cm/s)	
						Experimental	Predicted
4000	324	5.68	0.46	0.262	15.96	0.032	0.042
4000	324	3.79	0.69	0.243	15.43	0.018	0.023
4000	324	1.89	1.39	0.155	15.38	0.013	0.011
3000	243	5.68	0.46	0.262	15.96	0.036	0.034
3000	243	3.79	0.69	0.243	15.43	0.018	0.020
3000	243	1.89	1.39	0.155	15.38	0.009	0.009
2000	162	5.68	0.46	0.262	15.96	0.021	0.030
2000	162	3.79	0.69	0.243	15.43	0.017	0.019
2000	162	1.89	1.39	0.155	15.38	0.008	0.008
1000	81	5.68	0.46	0.262	15.96	0.015	0.024
1000	81	3.79	0.69	0.243	15.43	0.010	0.014
1000	81	1.89	1.39	0.155	15.38	0.003	0.005

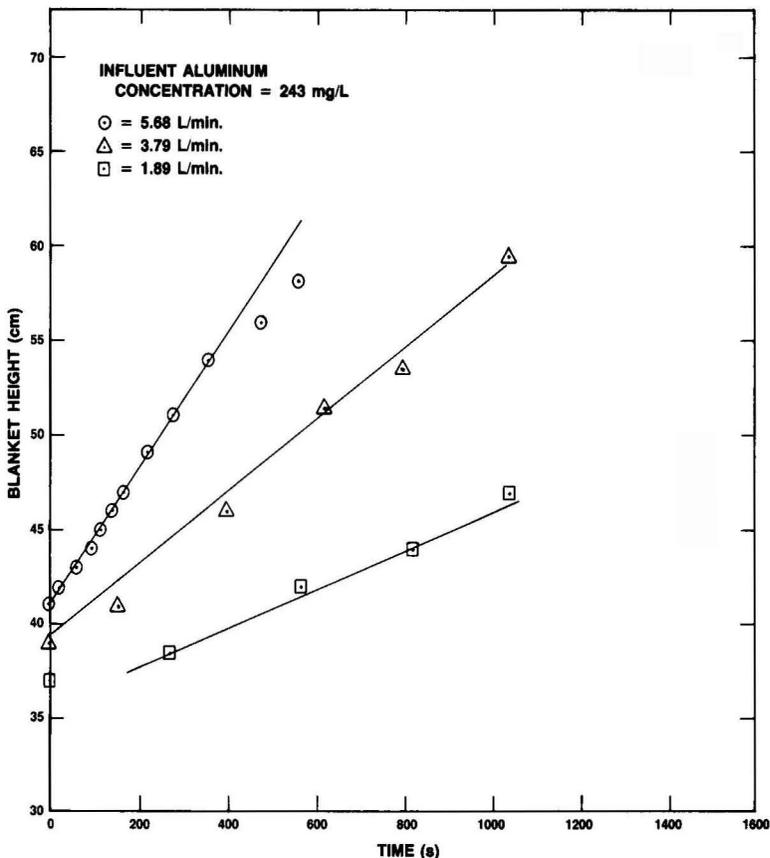


Figure 8. Data and model predictions of blanket height versus time, pilot scale apparatus, with influent aluminum concentrations of 243 mg/liter.

$x$  = distance from the bottom of the clarifier (cm)

#### Greek Letters

$\alpha$  = slurry viscosity parameter (unitless)  
 $\alpha^*$  = constant in Equation 7 (unitless)  
 $\alpha_z$  = constant in Equation 7 (unitless)  
 $\mu$  = viscosity  
 $\mu_w$  = viscosity of water (Poise)  
 $\mu_{H_2O}$  = density of water, (g/cm<sup>3</sup>)  
 $\mu_{sl}$  = slurry density (g/cm<sup>3</sup>)  
 $\Delta\rho$  = (floc density) - (water density)

#### Literature Cited

- U.S. Environmental Protection Agency, "Controlling Pollution from the Manufacturing and Coating of Metal Products," EPA 625/3-77-009.
- Metcalf and Eddy, Inc., "Wastewater Engineering: Treatment Disposal Reuse," McGraw-Hill Book Co., New York, 2nd edition (1969), Chapter 6.
- Graves, E. C., K. B. Schnelle, Jr., and D. J. Wilson, *Sep. Sci. Technol.* **16**, 263 (1981).
- Strang, R. M., Ph. D. Dissertation, Vanderbilt University (1982).
- Graves, E. C., K. B. Schnelle, Jr., and D. J. Wilson, *Sep. Sci. Technol.* **14**, 923 (1979).
- Wilson, D. J., E. C. Graves, and K. B. Schnelle, Jr., *Sep. Sci. Technol.* **15**, 1429 (1980).
- Strang, R. M., K. B. Schnelle, Jr., and D. J. Wilson, *Sep. Sci. Technol.* **18**, 253 (1983).
- Stumm, W. and J. J. Morgan, *J. Amer. Water Works Assoc.* **54**, 971 (1962).
- Graves, E. C., Ph. D. Dissertation, Vanderbilt University, Nashville, Tennessee (1979).
- Schroeder, P. R., "Pilot Reactor-Clarifier; Laboratory Analysis of Design, Construction, and Operation," unpublished M. S. paper, Vanderbilt University, Nashville, Tennessee (1978).

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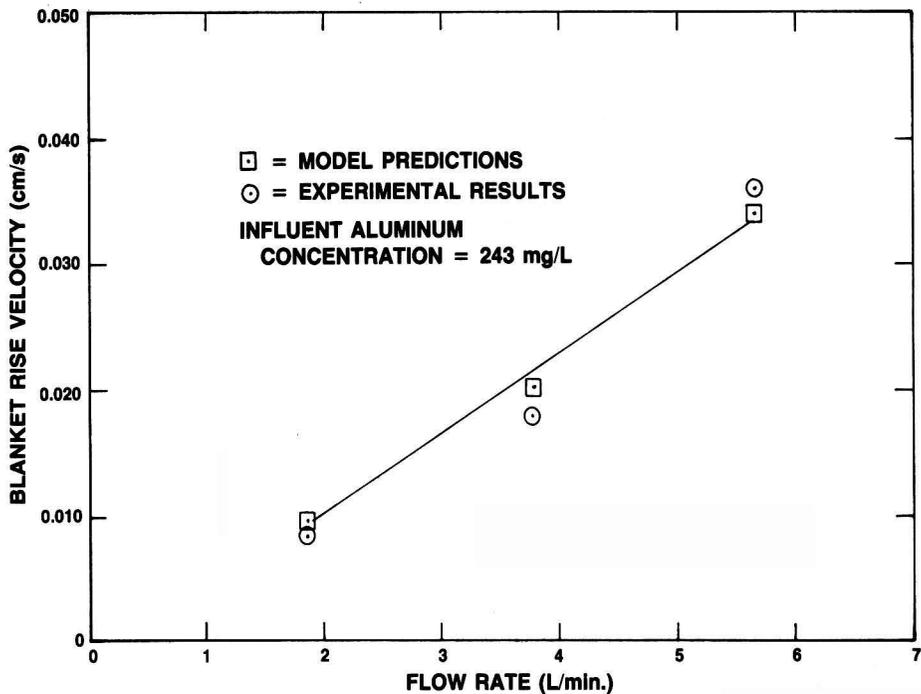


Figure 9. Data and model predictions of blanket rise velocity versus flow rate, pilot scale apparatus, with influent aluminum concentration at 243 mg/liter.

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# Separation of Metals in Wastewater Sludge by Centrifugal Classification

**Data for centrifugal classification can be suitably correlated by an easily correlated recovery factor, which can be calculated from a single replicated data point.**

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Municipal wastewater treatment and many industrial processes produce aqueous sludges as waste products. Frequently, the principal components of these sludges are innocuous metal hydroxides or organic substances contaminated with a small amount of toxic or otherwise undesirable substances. Municipal wastewater sludge is a good example. Not considering its content of pathogenic organisms, whose impact can be reduced by proper disposal procedures, it primarily consists of human feces, paper fiber, laundry residues, food residues from garbage grinders, with varying quantities of road dirt and industrial wastes. The great bulk of the solid content is harmless or beneficial; toxic contaminants are generally present only in trace amounts. There would be substantial benefit if these trace substances could be removed economically. Extraction with organic solvents or mineral acids is effective in removing toxic organic or inorganic contaminants. However, these procedures approximately double the cost of sludge treatment and disposal [1, 2], and so have not found any substantial use in upgrading municipal wastewater sludge to constructive use.

In their work at Lake Tahoe, California, with sludge produced in upgrading secondary effluent by lime treatment, Evans *et al.* [3] discovered that a solid-bowl continuous decanter centrifuge with an internal helical conveyor for solids removal (herein called a decanter centrifuge) separated the sludge into two fractions substantially different in composition. The primary constituent of the sludge was calcium carbonate, with lesser amounts of magnesium phosphate, calcium hydroxyapatite, and organic solids. Evans *et al.* [3] found that the calcium carbonate was concentrated in the solids in the cake, whereas the magnesium and phosphate compounds were concentrated in the solids in the centrate. Consequently, instead of just wasting a portion of the cake to bleed off impurities, they deliberately operated their centrifuge inefficiently, losing the undesirable phosphates and magnesium compounds in the centrate. The cake, which was enriched in calcium carbonate, was returned to CaO and reused. The centrate solids were subsequently collected by a second centrifuge using a polymer and discarded. This procedure improved the economics of their process because the lime concentration in the reburned product was increased, calcium carbonate losses were lower, and lime makeup was reduced.

Parker *et al.* [4] reported results of a similar investigation with a sludge produced by treatment of raw wastewater with lime. Organic solids were much higher in the sludge than were observed by Evans *et al.* Nevertheless, a similar degree of classification of recoverable calcium into the centrifuge cake occurred.

Analysis of information obtained from the Los Angeles County Water Pollution Control Districts (LACWPCD) showed that this effect also occurs with the heavy metals in sewage sludge [5]. At the time, the LACWPCD sludge was being centrifuged in a Bird decanter centrifuge without a polymeric conditioning agent. Recoveries of sludge in the cake were poor—on the order of 40 percent. Examination of data showed that concentrations of metals such as cadmium and lead were substantially higher in the centrate solids than in the cake solids.

The interesting results of these investigators suggested that centrifugal classification might prove to be a useful and cost-effective method for removing harmful substances from sewage sludge. Consequently, an investigation of this separation method was commenced at EPA's Municipal Environmental Research Laboratory in Cincinnati. The investigation was divided into three parts. First, published data of other investigators were examined to determine if there was a suitable means of correlating the degree of separation achievable with machine or process variables. Second, a pilot-scale investigation was commenced using sludge from Cincinnati's Mill Creek plant to determine if the LACWPCD classification results could be verified in another sludge, and third, LACWPCD records were investigated to determine whether more unpublished supporting data could be found. Results of these three phases of our investigation are presented in the following sections.

## CORRELATION OF CLASSIFICATION RESULTS

The most suitable information available at the time for testing a correlation method was the data of Evans *et al.* [3]. They worked with what was primarily a mineral sludge, which would not be expected to show large variations in characteristics with time. Most important, they obtained classification data over a range of cake recoveries. Cake recovery was varied by varying feed rate to the centrifuge over a limited range. Centrifuge bowl speed and speed of the conveyor for removing solids from the centrifuge were held constant (see below for description of a decanter centrifuge). Pool depth was varied but did not affect classification significantly.

The data obtained by Evans *et al.* have been replotted essentially in the same fashion as presented by these authors and are shown in Figure 1 for recalcinable calcium oxide. Percentage of the recalcinable calcium oxide that is recovered in the cake is plotted against percent of total solids recovered in the cake. The correlation procedure is useful but clearly several data points are required to get an

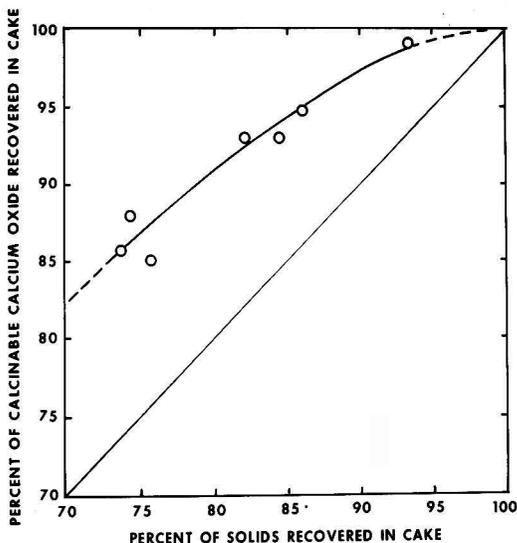


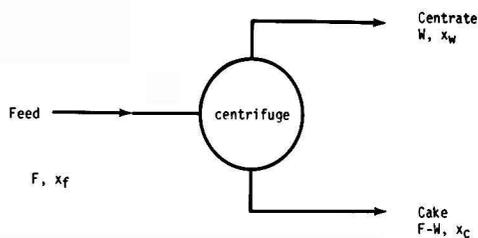
Figure 1. Correlation of recovery of a species (in this case, recalcinable CaO) with total solids recovery in the cake of a decanter centrifuge (from Evans *et al.*).

estimate of trends over a range of recoveries.

The superficial resemblance of the curve in Figure 1 to the familiar  $x$ - $y$  diagram used to present vapor-liquid equilibrium data [6] led to the thought that a pseudo-relative volatility would be reasonably constant over a substantial range of recovered solids. The pseudo-relative volatility, called here a "recovery factor" ( $f_r$ ), is calculated from the recoveries of a species and of total solids. Because for sewage sludge the "recovered" substances were concentrated in the centrate, recoveries in the centrate of solids and the various species of interest rather than recoveries in the cake were used. Nomenclature is shown in Figure 2.

The equation for the recovery factor, by analogy to the expression for relative volatility [6], is given by Equation 1:

$$f_r = \frac{R_a(1 - R)}{R(1 - R_a)} \quad (1)$$



$F$ ,  $W$ , and  $F-W$  are mass of suspended solids in feed, centrate, and cake.

$x_f$ ,  $x_w$ , and  $x_c$  are weight fraction (dry solids basis) of a species in the suspended solids in feed, centrate, and cake.

Figure 2. Representation of the centrifuge experiment, identifying the nomenclature for total flows and flows of any particular species into and out of the centrifuge.

where  $R_a$  = recovery of species  $a$  in centrate,  $Wx_w/Fx_f$   
 $R$  = recovery of solids in centrate,  $W/F$

Note that if  $R_a$  and  $R$  were recoveries in the cake, the recovery factor would be the reciprocal of  $f_r$ .

When the definitions of recoveries above are substituted into Equation 1 and combined with the material balance for the species around the centrifuge,

$$Fx_f = Wx_w + (F - W)x_c \quad (2)$$

Equation 1 reduces to a very simple form that is frequently useful in calculating  $f_r$ :

$$f_r = x_w/x_c \quad (3)$$

Equation 1 has been applied to the data of Evans *et al.* with the results shown in Table 1. Arithmetic average  $f_r$ 's have been used to calculate the recoveries,  $R_a$ , for the three species reported. Except for the three outliers noted, the average  $f_r$ 's represent the data well, as indicated by the agreement between calculated and measurable recoveries for the three species (column 2 versus column 4 in the table). The range of the total recoveries,  $R$ , is substantial (about 8 to 26 percent) but evaluation over a broader range would clearly be desirable.

The correlation approach used, if proven to be sufficiently general and usable over a broad range of recoveries, can greatly simplify collection of screening data to determine the value of centrifuged classification for a desired separation. Instead of establishing an entire recovery curve (e.g., Figure 1), it may be adequate to determine as few as one or two experimental points to indicate the utility of the approach. This potential was kept in mind in planning the experimental phase of the investigation.

## PILOT-SCALE STUDIES WITH SEWAGE SLUDGE

### Objectives

The objectives of this phase of the investigation were to establish the extent of classification that occurs in sewage sludge for a variety of trace metals, determine the

TABLE 1. COMPARISON OF MEASURED AND CALCULATED RECOVERIES (Evans *et al.*'s Data)

Species	Experimental Data		Calculated $f_r$	$R_a$ , Calcd. from $f_r$ -av.
	R	$R_a$		
PO <sub>4</sub>	0.24	0.90	27.8 <sup>1</sup>	—
	0.18	0.31	2.1	0.30
	0.16	0.29	2.2	0.27
	0.08	0.14	1.9	0.15
	0.07	0.11	1.7	0.13
			1.98 Ave.	
Mg	0.18	0.31	2.0	0.31
	0.16	0.29	2.2	0.28
	0.07	0.12	2.0	0.13
	0.08	0.04	0.5 <sup>1</sup>	—
			2.07 Ave.	
Ca	0.24	0.15	0.55	0.12
	0.26	0.14	0.47	0.13
	0.26	0.12	0.40	0.13
	0.14	0.05	0.34	0.06
	0.16	0.07	0.42	0.07
	0.18	0.07	0.36	0.085
	0.08	0.01	0.14 <sup>1</sup>	—
			0.42 Ave.	

<sup>1</sup> Outliers, not used in calculation of average  $f_r$ 's.

influence of the operating parameters of the centrifuge, and verify that the data obtained could be correlated over a broad range of variables by use of the "recovery factor" parameters.

### Materials and Methods

A pilot-scale decanter centrifuge (Sharples Model P-660, 0.15 m diam.), installed at the EPA's Test and Evaluation Facility at Cincinnati's Mill Creek Sewage Treatment Plant, was used for this investigation. Mill Creek's undigested primary sludge was used for all experiments. Composition range of heavy metals in this sludge during the experimental program is shown in Table 2. The wastewater has a substantial industrial contribution, but metals concentrations are not unusually high. Variables investigated were centrifuge bowl speed (RPM), depth of the liquid pool in the centrifuge bowl (PD), differential speed between bowl and conveyor (DELTA), and sludge feed rate (GPM). All other machine variables and sludge properties were held as constant as possible. A schematic drawing of a decanter centrifuge is shown in Figure 3. The centrifuge tested was a countercurrent flow machine—the solids thrown against the inner wall of the bowl were moved by the conveyor opposite to the direction of the liquid flow.

The feed sludge for the experiments was prethickened to about 2-4 percent solids, and screened to remove particles that might clog openings in the small decanter centrifuge. The screened sludge was stored in a 30.3-m<sup>3</sup> tank and was mixed with an air sparger to produce a uniform composition and prevent septicity. The tank contents provided the material for a day's operation, about 6-8 runs. No new sludge was added to the tank during an operating day. Input flow to the centrifuge passed through a grinder and a magnetic flow meter. No conditioning agents to improve particle collection were used. A schematic diagram of the sludge feeding system is shown in Figure 4.

To commence a run, the centrifuge was operated at the desired conditions for about 15 minutes to achieve steady state. Then the test period of about 5 to 15 minutes commenced, during which time all cake and centrate were collected. Samples of the cake and centrate were taken for determination of concentration of total solids and the following metals: cadmium, lead, zinc, copper, nickel, calcium, and iron. Sludge samples were digested with nitric/perchloric acid as has been described elsewhere [7] and metals concentrations were determined by atomic absorption spectrophotometry.

Balances for total mass and for individual metals were carried out. Material balance results for Experiment 1 (see below) are shown in Table 3. Material balances were good for total mass and total solids. Material balance for metals showed substantial variability, even though each measurement of a solids composition was an average of four or more grab samples. Metals analyses were conducted on composited samples. The relatively high standard deviations of the ratio of output to input for the metals indicate

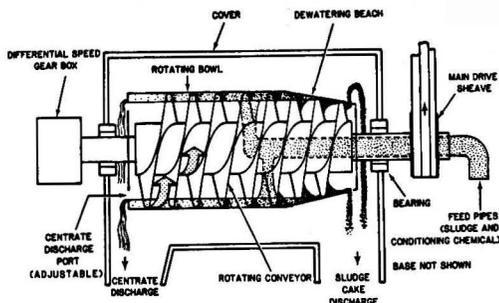


Figure 3. Continuous countercurrent solid bowl centrifuge.

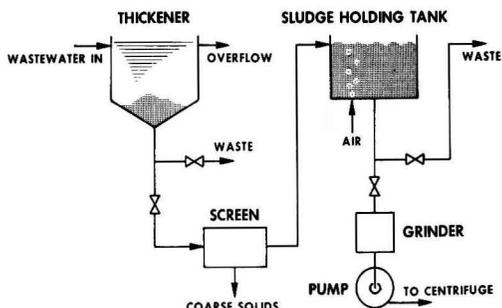


Figure 4. Sludge feeding system.

that compositions were fluctuating or that insufficient time was allowed for arriving at steady state. To eliminate the latter possibility, future experiments should use longer time periods to achieve steady state, and the sample collection period at steady state should be longer.

The effect of the poor material balances for some of the metals on the results is not certain. The calculations of  $f_r$  were made by Equation 3, which only uses the output compositions; consequently, variations in  $f_r$  might not reflect the uncertainty in the material balances. The consistency of the results (see below) indicates that the results are actually better than the material balances might indicate.

### Experimental Design

For maximum efficiency, the experiments conducted with the centrifuge were factorial designs [8]. Experiment No. 1 was planned as a  $3 \times 2 \times 2 \times 2$  factorial experiment (three bowl speeds, two pool depths, two differential

TABLE 2. CONCENTRATIONS OF HEAVY METALS IN CINCINNATI'S MILL CREEK RAW PRIMARY SLUDGE DURING CENTRIFUGATION EXPERIMENTS

	Concentrations (mg/kg, dry solids basis)		
	Low	High	Median
Cadmium	12	81	38
Lead	130	731	476
Copper	1,390	2,280	1,510
Nickel	240	680	380
Zinc	900	1,600	1,390
Calcium	8,400	28,900	14,100
Iron	11,600	21,600	15,300

TABLE 3. AVERAGE AND STANDARD DEVIATION(S) FOR THE RATIO OF MASS OUTPUT TO INPUT (O/I) FOR CENTRIFUGE EXPERIMENTS

No. of Measurements	Experiment 1		Experiment 2		All Experiments	
	Ave O/I	s	Ave O/I	s	Ave O/I	s
Total Mass					0.96	0.045
Total Solids					0.91	0.14
Elements*						
Cd	1.05(2)	0.28	0.89(1)	0.21		
Pb	1.14	0.29	0.97(2)	0.38		
Zn	0.98	0.25	0.95(1)	0.18		
Cu	0.99	0.17	0.99(2)	0.22		
Ni	1.00	0.15	1.01(1)	0.18		
Ca	1.00	0.24	1.03(2)	0.29		
Fe	0.99	0.16	1.11(2)	0.26		

\* ( ) indicates number of outliers not included in the average.

speeds, and two flow rates) replicated once. This large experiment necessarily extended over a period of many days. Procedures were followed which attempted to minimize the expected variations in sludge composition. The procedures for collecting sludge feed outlined in the preceding section were followed, which maintained sludge composition and quality constant during a single day. A complete block of tests, comprising a replicated  $2 \times 2$  sub-experiment (differential speed  $\times$  flow rate), was then run in a single day. As soon as possible (but not the same day), another sub-experiment was conducted at the second pool depth. Finally, this subset, now a  $2 \times 2 \times 2$  experiment, was repeated for each of the two remaining bowl speeds. Unfortunately, examination of the data leads to the conclusion that the effects of pool depth and bowl speed are confused with day-to-day changes in sludge and cannot be evaluated. The centrifuge machine settings and sludge feed conditions for this experiment are presented in Table 4.

In order to test the effect of bowl speed on the same sludge, the centrifuge was modified by installation of a variable speed drive, which permitted quick changes in bowl speed. A second factorial experiment (Experiment 2) using the same variables as before (two pool depths, two differential speeds, three bowl speeds, and two feed rates) was carried out except that there were no replicates. On a single day, six runs could be made, varying bowl speed and flow rate, at fixed differential speed and fixed pool depth. Then, these six runs were repeated on another day at the second differential speed. The two sets of six runs were then repeated at a new pool depth. Machine and sludge feed conditions are shown in Table 4. Because pool depth and differential speed were held constant during a day, their effects are confused with day-to-day changes in the sludge.

A third set of experiments designed to establish the response surface for the operating variables was in progress when the gear train of the centrifuge was damaged, terminating all further experiments. Unfortunately, experiments in which the effect of pool depth was determined on the same sludge were never run. However, cumulative information from the three sets of experiments presents a reasonable picture of effect of variables on classification of metals.

#### Analysis of Experimental Results

**Interpretation of Normalized Data.** As noted earlier, experimentation soon showed that day-to-day variation in the sludge was substantial. Comparison of results obtained

on different days were thus confounded with random unknown effects of changes in sludge characteristics. To allow interpretation of Experiments 1 and 2 in their entirety, each day's results, which were complete sub-experiments, have been normalized by calculating  $f_r$  for each test, calculating an arithmetic average  $f_r$ , and normalizing by dividing each  $f_r$  by the average. Normalized  $f_r$ 's are indicated by the symbol  $n - f_r$ . Naturally, the overall average of the normalized  $f_r$ 's for a day's tests must equal unity; thus, any variables that did not vary within a day (bowl speed and pool depth for Experiment 1, differential speed and pool depth for Experiment 2) show zero effects, although their interactions with other variables are not zero.

Effects of variables and interactions on  $f_r$  determined from results of Experiment 1 are presented in Table 5. Increase in flow rate (GPM) increases  $f_r$  for all but one metal and the increase is statistically significant for Cd and Ca. Differential speed (DELTA) effects are small and fluctuate in direction, indicating only random error. The effect of pool depth (PD) is unknown but its interaction with flow rate appears to be important—it is substantially significant for three metals. A high pool depth reduces the improvement in  $f_r$  produced by increased feed rate. The nature of this interaction suggests that a combined variable, PD/GPM, which is proportional to time of exposure of sludge to the centrifugal field, might be appropriate.

Results of Experiment 2 are presented in Table 6. Data have been normalized as for Experiment 1. Increasing centrifuge speed (RPM) increases  $n - f_r$  significantly for Cd and Pb, but the effect is much less and not significant for other metals. Flow rate (GPM) effect is substantial and quite similar to results obtained for Experiment 1.

Significant interactions did not follow any regular pattern in Experiment 2. In one case, the PD  $\times$  GPM interaction was significant and in the same direction as for Experiment 1. Average  $f_r$ 's are lower in Experiment 2 than in Experiment 1. A difference is to be expected because the experiments were run nearly a month apart.

In the experiments, significant effects occur more frequently for metals showing the most classification into the centrate (Cd and Pb) and into the cake (Ca). This behavior is reasonable. If, for example, a metal is only slightly classified, as indicated by an  $f_r$  near unity, no appreciable effect of machine variables on  $f_r$  should be anticipated.

The results of the factorial analysis show that the use of the recovery factor is an extremely useful tool for correlation centrifugal classification results. Results can be expressed by a single parameter,  $f_r$ , which is only slightly affected by the operating conditions of the centrifuge.

TABLE 4. MACHINE AND SLUDGE FEED CONDITIONS FOR EXPERIMENT 1 (5/29-7/22) AND EXPERIMENT 2 (8/13-8/28)

Date	Replications/ Tests	Machine Conditions				Feed Conditions	
		Speed (1000 RPM)	Pool Depth	Differential Speed	Flow Rate** (GPM)	Solids Content (%)	Range of Total Solids Recoveries
Experiment 1							
5/29	2/8	5.0	1	Min., Max.	2, 5	1.28	0.33-0.50
6/3	2/8	5.0	4	Min., Max.	2, 5	2.38	0.22-0.50
6/9	2/8	3.1	4	Min., Max.	2, 5	1.27	0.29-0.54
6/11	2/8	3.1	1	Min., Max.	2, 5	1.85	0.30-0.60
7/17	2/8	1.9	1	Min., Max.	2, 5	2.93	0.52-0.82
7/22	2/8	1.9	4	Min., Max.	2, 5	2.34	0.35-0.58
Experiment 2							
7/29*	1/6	1.9, 3.1, 5	1	L	2, 6	2.25	0.52-0.80
8/13	1/6	1.9, 3.1, 5	1	L	2, 5	2.34	0.38-0.65
8/20	1/6	1.9, 3.1, 5	1	H	2, 5	1.78	0.35-0.80
8/26	1/6	1.9, 3.1, 5	4	L	2, 5	1.55	0.16-0.68
8/28	1/6	1.9, 3.1, 5	4	H	2, 5	1.88	0.19-0.56

\* The 7/29 run was incomplete. It was not used to compute the results of the factorial experiment.

\*\* S.I. Conversion: GPM  $\times$  0.0631 = LPS (liters/sec).

TABLE 5. EFFECT OF MACHINE VARIABLES ON RECOVERY FACTOR — EXPERIMENT 1

Metal	Average $f_r$	Magnitude of Effects on Normalized $f_r$		
		Main Effects		Two Factor Interactions**
		Delta	GPM	PD × GPM
Cd	2.77	-0.06	0.24*	-0.15*
Pb	2.90	0.04	0.08	-0.22*
Cu	1.86	-0.07	0.04	—
Ni	1.60	-0.09	0.08	—
Zn	1.80	-0.03	0.08	—
Ca	0.96	-0.06	0.17*	-0.21*
Fe	1.02	0.14	-0.03	—

\* Effect was significant at 95% level or greater.  
 \*\* Only significant interactions are shown.

**Graphical Interpretation of Data.** Statistical analysis of the factorial experiments is a very powerful help in analysis, but comprehension is aided when the data can be presented graphically. Fortunately, the data can be illustrated graphically in a way that proves to give confidence in the use of  $f_r$  as a correlating parameter. The definition of  $f_r$  suggests that, if Equation 1 fits the data, a straight line through the origin will be obtained if  $R_n/(1 - R_n)$  is plotted against  $R/(1 - R)$ . These plots are illustrated in Figure 5 using a portion of the data obtained for cadmium in Experiment 1. The raw data before normalization have been used. The three sets of curves show that straight lines represent the data well, indicating that the assumption of a constant  $f_r$  is not unreasonable. The effect of flow rate (GPM) discovered in the factorial analysis (see Table 5) is not apparent in these diagrams. The residual error causes enough variation to obscure the effect of flow rate. The normalized standard deviation in Experiment 1 for cadmium was 0.22. This means that there is a large scatter in the data—about 32 percent of measurements of  $n - f_r$  would be expected to fall outside of the one sigma range of  $\pm 0.22$ . It is easy to see why the normalized effect of flow rate, 0.23, could go unobserved without the factorial analysis. It was only because the large experiment (Experiment 1 contained 24 runs) reduced the residual error to a low value so that the machine variable effects could be seen.

Recovery factors determined as slopes of least square lines of the daily test data, plotted as  $R_n/(1 - R_n)$  vs.  $R/(1 - R)$ , were calculated for all of the tests for all of the metals. These results are shown in Table 7. The values of  $f_r$  for each metal fluctuate substantially with time. The major part of this fluctuation was probably due to changes in the sludge, although changes in the centrifuge, such as wear

on the helical conveyor for removing sludge, could account for some of the changes.

**Data Needed to Predict Degree of Classification.** If it is desired to test whether centrifugal separation offers any advantage for separating components of a slurry, the large standard deviations such as experienced in our work make it difficult to make accurate predictions, but simplify the experimental task. Our experiments show that effects of machine variables, although measurable in some cases, are not large compared to the experimental inaccuracy in determining  $f_r$ . Similarly, marked changes in  $f_r$  appear not to occur as  $R$  changes (see Figure 5). Consequently, to get a reasonable estimate of  $f_r$ , a few runs can be made, changing a few adjustments in machine variables and feed rate to bracket the desired  $R$ , and an average value and standard deviation in the  $f_r$  determined. A very large experiment is needed to define the relatively small effects of machine variables. At least for a non-consistent feedstock such as sewage sludge, the relatively large changes in  $f_r$  that occur with time make it pointless to excessively refine the estimate of  $f_r$ .

**LONG TERM EXPERIENCE AT LOS ANGELES**

As noted earlier, the LACWPCD had been operating decanter centrifuges for a number of years without using polymers to enhance particle collection, and differences in concentrations of metals in centrate and cake had been observed. The correlation method developed here (use of  $f_r$ ) allows interpretation of the data and allows a comparison of data collected over a period of years.

The Los Angeles County data are from 1979 and earlier, at which time sludge was centrifuged in a Bird decanter centrifuge and the centrate was again centrifuged in solid-bowl basket-type centrifuges. Because no polymer was used in the decanter centrifuge and recovery of solids was poor, the second centrifugation was needed for efficient solids removal. Data are shown in Table 8, which gives composition of sludge feed, decanter centrifuge cake, and basket centrifuge cake. If it is assumed that all of the sludge solids in the centrate are removed in the basket centrifuge, it is possible to calculate fraction of solids recovered and a recovery factor for the elements and compounds listed in the table. The calculated recoveries scatter but indicate recoveries in the cake of 23 to 30 percent (77 to 70 percent solids are "recovered" in the centrate). The calculated separation factors are substantial for some metals (e.g., 4.5 for cadmium) and for the organic compounds listed. Actually, it was these data that encouraged us to believe that the separation achieved by Evans *et al.* [3] with tertiary slime sludge might occur with sewage sludge.

The Los Angeles County data, which were obtained on digested sludge, indicate better separations for most met-

TABLE 6. EFFECT OF MACHINE VARIABLES ON RECOVERY FACTOR — EXPERIMENT 2

Metal	Average $f_r$	Magnitude of Effects on Normalized $f_r$				
		Main Effects		Two-Factor Interactions**		
		GPM	RPM (1 to 3)	Delta × GPM	PD × GPM	GPM × RPM (1-2)
Cd	1.86	0.23*	0.28*	—	—	—
Pb	1.77	0.01	0.68*	-0.31	—	—
Cu	1.82	0.17	0.10	—	—	—
Ni	1.48	0.12	0.03	—	—	—
Zn	1.56	0.16*	0.05	—	—	0.26
Ca	0.83	0.40*	-0.06	—	-0.26	—
Fe	1.37	0.24*	0.16	—	—	—

\* Effect was significant at 95% level or greater.  
 \*\* Only significant interactions are shown.

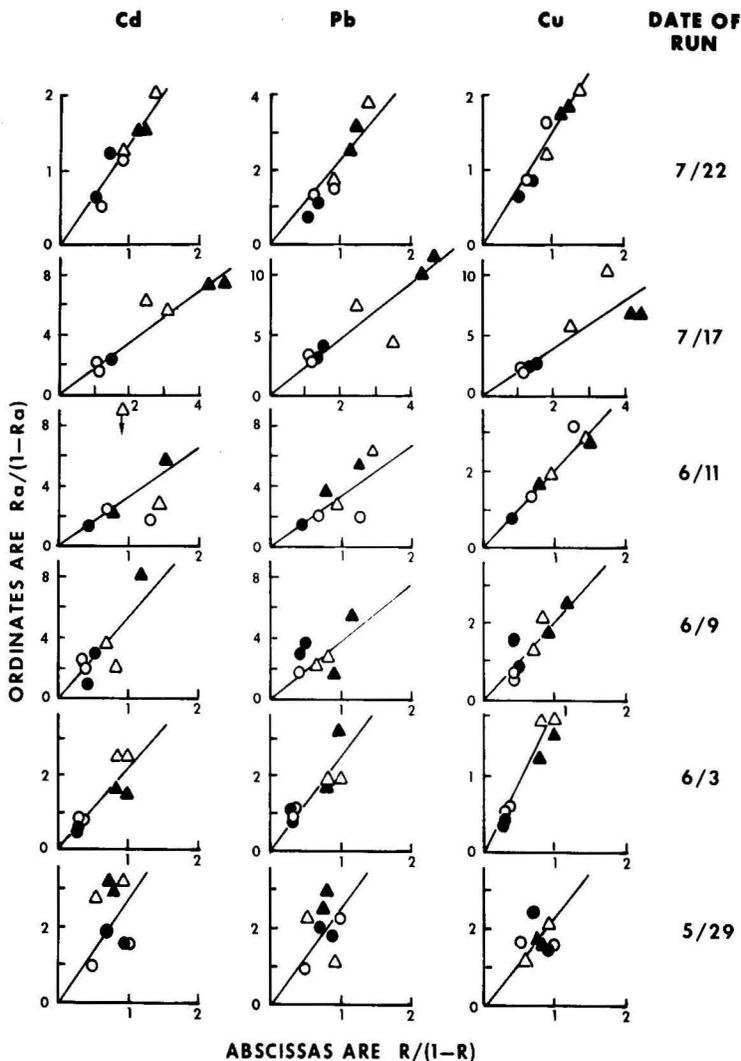


Figure 5. Comparison of  $R_a/(1-R_a)$  to  $R/(1-R)$  for cadmium, lead and copper (symbols:  $\circ$  = 2gpm,  $\Delta$  = 5 gpm; unshaded = low Delta, shaded = high Delta).

als than were obtained in the present investigation of raw undigested sludge, but were poorer for others, particularly for lead. The relative magnitudes of the  $f_r$ 's calculated from this study and from the Los Angeles data collected over about two years are given below:

	Cd >	Zn >	Ni >	Cu >	Pb
L.A.	(3.6)	(2.9)	(2.6)	(2.2)	(0.8)
	Pb >	Cd >	Cu >	Zn >	Ni
This Study	(3.2)	(2.8)	(1.9)	(1.8)	(1.7)

The differences in magnitude and relative position are substantial but not unexpected. Industrial mix of the two cities is different so the sources of the metals in the sludges differ. Los Angeles has a separate system whereas Cincinnati has a combined system (sewage contains storm runoff), the Cincinnati sludge was raw and Los Angeles' was digested. It can be said that most of the heavy metals will be classified into the centrate, but magnitude and relative position will have to be established by experiment.

Data in Table 8 show that organic substances such as pesticides and PCB's are classified into the centrate. This

is an interesting and highly desirable occurrence. In other separation techniques such as extraction, it would be expected that two extractions would be needed to remove metals and organic chemicals: an aqueous acid extraction for metals and an organic solvent extraction for the organic compounds. Centrifugal classification evidently removes a large portion of both in a single step.

One extremely important question is the reproducibility of the phenomena. Our data indicate substantial fluctuations with time (Table 7). Fortunately, Los Angeles has also provided us with long term data [9] from which  $f_r$ 's could be calculated that indicate surprising consistency with time. These data were provided in the form shown in Table 8 and recovery factors were calculated in the same manner as shown in the table. Monthly values of  $f_r$  for cadmium over the three-year period are plotted in Figure 6. Means and standard deviation of  $f_r$ 's are shown on the figure. There are no trends that indicate low recovery factors for long periods of time. Standard deviations are not excessive. Similar experience would likely be encountered in other cities, barring some drastic change in the industrial mix.

TABLE 7. CALCULATED RECOVERY FACTORS ( $f_r$ ) FOR EXPERIMENTS 1 AND 2

Date of Run	Metal						
	Cd	Pb	Zn	Cu	Ni	Ca	Fe
5/29	2.78	2.50	1.60	2.12	1.74	1.94	0.92
6/3	2.22	2.48	1.58	1.72	1.57	0.50	0.95
6/9	5.27	3.82	2.07	2.16	1.48	0.91	1.04
6/11	3.30	3.27	2.12	2.03	1.52	0.79	0.84
7/17	2.07	2.27	1.59	1.88	1.36	0.78	0.90
7/22	1.36	2.25	1.76	1.51	1.76	0.81	1.12
7/29*	1.86	5.10	1.77	1.91	1.77	1.06	1.05
8/13	2.73	1.87	1.92	2.34	1.89	1.53	1.98
8/20	2.05	1.10	1.27	1.75	1.15	1.23	1.76
8/26	1.49	2.50	1.47	1.53	1.44	0.73	1.02
8/28	1.41	1.01	1.29	1.58	1.27	0.51	0.67
Arithmetic Average	2.41	2.56	1.68	1.78	1.54	0.98	1.11
Std. Deviation	1.13	1.17	0.28	0.41	0.23	0.44	0.40

\* This experiment was not complete and was not used in the factorial experiment calculations.

**DISCUSSION OF RESULTS AND PROCESS POTENTIAL**

The results clearly show the value of the correlating method developed. The utility of the recovery factor,  $f_r$ , in correlating classification data is impressive. A minimum of data is needed to determine  $f_r$ . Once it is known, material balance calculations can be made quickly to assess the utility of the method of separation.

The method is empirical and should not be extrapolated over a wide range of compositions or a wide range of recoveries. It can be demonstrated that, for example, at a  $f_r$  of 3.0, which is reasonable in light of the values determined in the above experiments, if  $R$  equals 0.5, impossible values of  $x_m$  (i.e., greater than one) will be obtained if  $x_j$  is greater than 0.667.

The potential of the process for upgrading sludge has one handicap—the sludge cake is reduced in heavy metal content, and the centrate is increased. The situation would be better if the cake solids were increased in heavy metals and the centrate solids reduced in metals. Then, an obvious application would be ocean disposal or land disposal. A small amount of “dirty” cake could be landfilled or carefully incinerated while the bulk of the centrate, probably

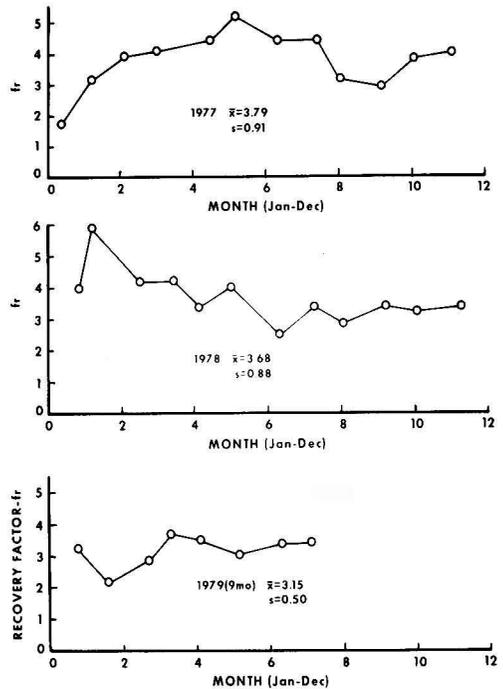


Figure 6. Variation in  $f_r$  for cadmium, obtained at LACWPCD over a three-year period.

after thickening, could be used on the land or disposed with much less than half the environmental impact of the total sludge.

Despite the handicap, it appears that cost-effective ways to use the separation method can be devised. One application is in a plant using dedicated disposal to get rid of a sludge higher in metals than is suitable for use on land. If the sludge were centrifugally classified, a “clean” cake could be produced that could be used on farmland at low disposal cost. The “dirty” centrate could be disposed to the dedicated land. Since organic loading would be much reduced, the capacity of the disposal site would be increased.

TABLE 8. CLASSIFICATION OF METALS AND ORGANIC COMPOUNDS BY DECANTER CENTRIFUGES AT LOS ANGELES COUNTY (AUGUST 1977)

	Concentrations (mg/kg dry solids) <sup>1</sup>			Calculated Recovery of Solids in Cake	$f_r$ (= $x_m/x_c$ )
	Decanter feed ( $x_f$ )	Decanter cake ( $x_r$ )	Basket cake ( $x_m$ )		
As	23	9	25	0.12	2.8
Hg	7	6	7	0	1.2
Ag	42	19	49	0.23	2.6
Cd	59	16	72	0.23	4.5
Ni	400	170	460	0.21	2.7
Pb	980	1500	1300	<0	0.86
Cr	2000	570	2600	0.30	4.6
Cu	1200	520	1400	0.23	2.7
Zn	3400	1100	4400	0.30	4
DDT	12	3	9.3	<0	3.1
PCB	8.5	2.3	7.7	<0	3.3
ALL					
All Pesticides	12	3	9.3	<0	3.1
TICH <sup>2</sup>	19.5	5.5	17.0	0.3	3.1

<sup>1</sup> Symbols correspond to nomenclature in Figure 2.  
<sup>2</sup> TICH—Total identifiable chlorinated hydrocarbons.

Another potential application is for a community which would like to compost its sludge but which has a sludge with a high metals content. The cake could be upgraded by centrifugation and the centrate thickened and dried in lagoons for ultimate disposal in a landfill.

In principle, countercurrent staging would allow production of an ultra-clean cake and an ultra-dirty centrate. Unfortunately a stage would compromise a centrifuge and a mixer for reconstituting cake to a slurry. It is unlikely that the net reduction in cost of disposal would offset the cost of the added capital and operating expense of such a system.

## CONCLUSIONS AND RECOMMENDATIONS

Significant conclusions are as follows:

- 1) Data for centrifugal classification appear to be suitably correlated by an easily calculated recovery factor, which in principle can be calculated from a single data point. The factor is a function of machine settings but an average recovery factor can be used to predict recoveries of a specific element with reasonable accuracy. The recovery factor can be extrapolated over a modest range of metal concentrations and recoveries. Substantial random error is to be expected so a sufficient number of runs should be made to establish the standard error of the recovery factor.
- 2) The degree of classification as indicated by the recovery factor,  $f_r$ , is better at high sludge feed rate and high centrifuge speeds. The differential speed of the internal conveyor does not seem to be an important variable. The effect of pool depth was confounded with day-to-day variations in the sludge so it could not be determined. However, interactions of pool depth with sludge feed rate indicate that pool depth divided by feed rate, which is proportional to time in the centrifuge, is an important variable.
- 3) The degree of classification,  $f_r$ , for a metal fluctuates with time. However, data collected over a three year period at Los Angeles indicate that the degree of classification does not undergo serious changes in magnitude with time.
- 4) The selectivity of the method for separating desirable from undesirable substances is good. Most of the heavy metals as well as toxic organic compounds are classified into the centrate. The results obtained show encouraging possibilities for centrifugal classification of sludges.

Recommendations for future work are as follows:

- 1) Attempts should be made to relate the design parameters of centrifugees (e.g., concurrent *vs.* countercurrent flow; long bowl *vs.* short bowl) to the degree of separation achieved. It is very unlikely that the centrifuge used in these experiments is the optimum design. Investigation of several designs should be made. From the differences in performance observed, the characteristics that improve separation can be identified and an optimized design can be selected.
- 2) More work should be done with a variety of different sludges, particularly on sludges with high proportion of toxic organic compounds. The Los Angeles data show substantial classification but more supporting information is needed.

- 3) Chemical and mineral processing industries should give serious consideration to centrifugal classification as a relatively inexpensive unit operation that could reduce waste of valuable materials in spent slurries.

## LITERATURE CITED

1. McNulty, K. J. *et al.*, "Evaluation of Hot Acid Treatment for Municipal Sludge Conditioning," EPA-600/2-80-096, U.S. EPA (Aug. 1980).
2. Camp, Dresser, and McKee, Inc., "Engineering Assessment of Hot-Acid Treatment of Municipal Sludge for Heavy Metals Removal," EPA-600/2-82-014 (Mar. 1982).
3. Evans, D. R. *et al.*, "Advanced Wastewater Treatment as Practiced at Lake Tahoe," EPA No. 17010 ELQ (Aug. 1971), (NTIS No. PB 204525).
4. Parker, D. S. *et al.*, "Sludge Processing for Combined Physical-Chemical-Biological Sludges," EPA-R2-73-250 (July 1973).
5. LA/OMA Project Technical Report No. 3, "Municipal Sludge Characterization: City of Los Angeles, Sanitation Districts of Los Angeles County, County Sanitation Districts of Orange County, California (Aug. 1977).
6. Treybal, R. E., "Mass Transfer Operations," 3rd ed., p. 349, McGraw-Hill, N.Y. (1980).
7. Ganje, T. J., and A. L. Page, "Rapid Acid Dissolution of Plant Tissue for Cadmium Determination by Atomic Spectrophotometry," *At. Absorpt. Newsl.* 13, 131-134 (1974).
8. Davies, O. L., ed., "Design and Analysis of Industrial Experiments," Hafner Pub. Co., N.Y. (1956).
9. W. Garrison/R. Horvath (for Los Angeles County Water Pollution Control Districts), Personal Communication to C. A. Fronk (Jan. 4, 1982).



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# INDEX TO VOLUME 4

## Authors

**A**  
 Ahlert, R. C. . . . . 22  
 Anzenberger, Lynn . . . . . 155

**B**  
 Balfour, W. David . . . . . 199  
 Balinsky, A. M. . . . . 131  
 Barner, H. E. . . . . 125  
 Beisswenger, H. . . . . 125  
 Bever, Paul M. . . . . 1  
 Blacksmith, J. R. . . . . 14  
 Bremen, W. M. . . . . 46  
 Bricka, R. Mark . . . . . 187  
 Bouwer, Edward J. . . . . 43  
 Bozzelli, Joseph W. . . . . 229  
 Byers, W. D. . . . . 112

**C**  
 Canney, F. J. . . . . 171  
 Chartier, J. S. . . . . 125  
 Chestnut-Metzler, Suzanne . . . . 61  
 Cook, James A. . . . . 26  
 Cooper, M. W. . . . . 182  
 Corbo, Patricia . . . . . 22  
 Cotter, Jack E. . . . . 165  
 Cuddy, M. . . . . 100

**D**  
 Daughton, G. C. . . . . 252  
 Deitrich, M. J. . . . . 171  
 Demski, Richard J. . . . . 223  
 Drabkin, Marvin . . . . . 39  
 Drummond, Charles R. . . . . 26

**E**  
 Ecklund, Bart M. . . . . 199  
 Eldridge, John W. . . . . 78  
 Elton, Richard L. . . . . 168, 182  
 Endicott, Douglas D. . . . . 105

**F**  
 Farrell, Joseph B. . . . . 269  
 Feeley, Thomas J. . . . . 26  
 Feldman, Lawrence . . . . . 178  
 Fjeldahl, Lanay . . . . . 212

Frankel, Irwin . . . . . 39  
 Fronk, Carol Ann . . . . . 269  
 Fogler, H. Scott . . . . . 239

**G**  
 Gibbs, S. J. . . . . 259  
 Gross, Randy L. . . . . 119  
 Gulari, Erdogan . . . . . 239  
 Gurol, M. D. . . . . 46

**H**  
 Harrison, D. P. . . . . 131  
 Hendrickson, J. G. . . . . 33  
 Hill, Donald O. . . . . 187  
 Holden, T. E. . . . . 46  
 Huang, Ching R. . . . . 229  
 Hwang, Seong T. . . . . 141

**J**  
 Jarvis, Katherine . . . . . 61  
 Jefcoat, I. Atley . . . . . 217  
 Jones, B. M. . . . . 252  
 Joubert, James I. . . . . 223

**K**  
 Kenson, R. E. . . . . 161  
 Kent, R. T. . . . . 182  
 Khan, Shahab R. . . . . 229  
 Kittrell, Jeffrey A. . . . . 78  
 Klinzing, George E. . . . . 1  
 Kocornock, D. J. . . . . 45  
 Kumar, Ashok . . . . . 85

**L**  
 Langlois, G. W. . . . . 252  
 Lunney, Phillip D. . . . . 203

**M**  
 MacKoul, L. J. . . . . 100  
 Mann, M. D. . . . . 33  
 Malow, Monroe . . . . . 151  
 Mastroianni, M. L. . . . . 7  
 McMurty, David C. . . . . 168  
 McTernan, W. F. . . . . 145  
 McVeigh, Thomas . . . . . 212

Miller, Ronald D. . . . . 26  
 Morton, C. M. . . . . 112  
 Myers, Tommy E. . . . . 187

**N**  
 Nelson, T. P. . . . . 14  
 Noceti, Richard P. . . . . 26  
 Nolan, Tim . . . . . 239

**P**  
 Patrick, David R. . . . . 20  
 Prahacs, S. . . . . 94

**R**  
 Randall, J. L. . . . . 14  
 Randall, T. L. . . . . 171  
 Rappe, Gerald C. . . . . 56  
 Reible, D. D. . . . . 131  
 Roberts, Louis R. . . . . 12  
 Rochelle, S. G. . . . . 7

**S**  
 Sakaji, R. H. . . . . 252  
 Santoleri, Joseph J. . . . . 246  
 Schipper, M. . . . . 182  
 Schmidt, Charles E. . . . . 199  
 Schmidt, H. W. . . . . 125  
 Schnelle, Jr., K. B. . . . . 259  
 Schnelle, K. D. . . . . 259  
 Schultz, Jerome S. . . . . 239  
 Siegel, R. D. . . . . A3  
 Silverberg, Ira . . . . . 65  
 Springer, Charles . . . . . 203  
 Srinivasan, Keeran R. . . . . 239  
 Steinberg, Meyer . . . . . 69  
 Strachan, William . . . . . 269  
 Strakey, Joseph P. . . . . 223

**T**  
 TerMaath, Stephen G. . . . . 119  
 Thibodeaux, Louis J. . . . . 203  
 Thomas, Suzanne T. . . . . 85

<b>W</b>	
Wagner, N. J. ....	136
Wang, C. C. K. ....	52
Weber, Walter J. ....	105
Wetzel, D. M. ....	131

Wiley, G. ....	100
Williams, S. L. ....	145
Willms, R. S. ....	131
Wilson, David J. ....	259
Wilson W. G. ....	33
Wiltse, J. ....	100

<b>Y</b>	
Yeh, James T. ....	223
<b>Z</b>	
Zimmerman, John ....	212

# Titles

<b>A</b>	
Alkylate Sludge Reuse Potential	165
Anaerobic Treatment of Concentrated Industrial Wastewater	22
Analysis of High Pressure, Multi-phase, Batch Reactor Data	131
Application of Circulating Fluid Bed Technology to the Combustion of Waste Material	125

<b>C</b>	
Case History of a Major Nitric Acid Spill	212
Combined SO <sub>2</sub> /NO <sub>x</sub> Removal from Flue Gas	223
Computation of Ground Level Concentration at Coastal Sites	85
Control of Air Emissions from Kraft Recovery Furnaces by Wet Scrubbing	94

<b>D</b>	
Design and Implementation of Groundwater Recovery Systems	182
Design and Operating Problems of Hazardous Waste Incinerators	246
Designing a Synthetic Fuel Plant for Low Sulfur Emissions	65

<b>E</b>	
Effect of Ozonation and UV Irradiation on Biorefractory Organic Solutes in Oil Shale Retort Water	252
Effects of Waste-Oil Contamination	61
Environmental Protection Agency's Regulatory Practices: The Impact of a Holistic Approach, The	155
Environmental Protection Agency's Risk Management Policy	20

<b>F</b>	
Fates of Contaminants During Treatment of H-Coal Process Wastewaters	26
Field Evaluation of Volatile Organic Compound Removal Efficiency for Full Scale Carbon Adsorption Systems	14

<b>G</b>	
Gasifier Wastewater Treatment: Phase I. Cooling Tower Assessment	33

<b>H</b>	
Hazardous Waste and the Common Law Theories of Liability	52
Hazardous Waste Characterization Extraction Procedures for the Analysis of Blast-Furnace Slag from Secondary Lead Smelters	225

<b>I</b>	
Improvements in Acetone Adsorption Efficiency	7

<b>L</b>	
Liquid Phase Mass Transfer Coefficients for Surface Impoundments	203
Lumped-Parameter Modeling of Multicomponent Adsorption in the Treatment of Coal-Conversion Wastewater by GAC	105

<b>M</b>	
Maleic Anhydride via Butane Oxidation	151
Mathematical Model of Settling Velocity Enhancement by Kinetic Control, A	259
Measurement of Fugitive Volatile Organic Emission Rates	199
Model Prediction of Volatile Emissions	141
Modeling Ammonia Gas Transport from Solidified Hazardous Waste	187

<b>N</b>	
New Approach to In-Situ Treatment of Contaminated Groundwaters, The	168
New Sludge Destruction Process	56
Novel Catalyst Preparation Method for NO <sub>x</sub> Control	78

<b>O</b>	
Oxidation of 2-Chlorophenol Using Ozone and Ultraviolet Radiation	229

Oxidation of Cyanides in Industrial Wastewaters by Ozone	46
--	----

<b>P</b>	
Packed Tower Aeration Strips Trichloroethylene from Groundwater	119
Process Simulation of Flue-Gas Desulfurization Systems with Organic Solvents	1

<b>R</b>	
Recovery and Reuse of Solvents from VOC Air Emissions	161
Recovery, Disposal and Reuse of CO <sub>2</sub> for Atmospheric Control	69
Removal of Trace Organics from Water by Sorption onto Natural and Synthetic Materials, The	239
Removing VOC from Groundwater; Pilot, Scale-up, and Operating Experience	112
Role of Environmental Site Assessment in Reducing Lender Risk in Massachusetts, The	178

<b>S</b>	
Secondary Utilization of Trace Halogenated Organic Compounds in Biofilms	43
Separation of Metals in Wastewater Sludge by Centrifugal Classification	269
Survey of Research on Environmental Pollution—Its Sources, Fate, Effects and Control	217

<b>T</b>	
Thermal Regeneration of Granular Activated Carbon	136
Treating Contaminated Returned Condensate at a New England Paper Plant	100
Treatment of an In Situ Oil Shale Retort Water	145

<b>W</b>	
Wastewater Treatment Systems for Synthetic Fuels Plants Based on Peat and Oil Shale	39
Wet Air Oxidation of Hazardous Organics in Wastewater	171

# Subjects

<p><b>A</b></p> <p><b>Acid</b> nitric .....212</p> <p><b>Adsorption</b> acetone .....7 carbon .....14 multicomponent.....105</p> <p><b>Aeration</b> .....119</p> <p><b>Air</b> emissions .....94, 161 oxidation (wet) .....171</p> <p><b>Alkylate Sludge</b> .....165</p> <p><b>Ammonia Gas</b> .....187</p> <p><b>Anaerobic Treatment</b> .....22</p> <p><b>Anhydride</b> maleic .....151</p> <p><b>Atmospheric Control</b> .....69</p> <p><b>B</b></p> <p><b>Batch Reactor Data</b> .....131</p> <p><b>Biofilms</b> .....43</p> <p><b>Biorefractory Organic Solutes</b> .....252</p> <p><b>Butane Oxidation</b> .....151</p> <p><b>C</b></p> <p><b>Carbon Dioxide</b> .....69</p> <p><b>Catalyst</b> .....78</p> <p><b>Centrifugal Classification</b> .....269</p> <p><b>Chlorophenol</b> .....229</p> <p><b>Clay (Modified)</b> .....239</p> <p><b>Combustion</b> .....125</p> <p><b>Contaminants</b> .....26 carbon dioxide .....69 returned condensate.....100 waste oil.....61</p> <p><b>Contaminated Groundwater</b> .....168</p> <p><b>Cooling Tower</b> assessment.....33</p> <p><b>Cyanides</b> .....46</p> <p><b>D</b></p> <p><b>Design</b> .....65, 182, 246</p> <p><b>Desulfurization</b> flue gas .....1</p> <p><b>Dioxins</b> .....239</p> <p><b>E</b></p> <p><b>Efficiency</b> adsorption .....7 removal .....14</p> <p><b>Emissions</b> .....94 control.....94 low sulfur .....65 voc air .....161 volatile .....141 volatile organic rates .....199</p> <p><b>Environmental Pollution</b> .....217</p> <p><b>Environmental Protection</b> Agency .....20, 155</p> <p><b>Environmental Site</b> Assessments .....178</p> <p><b>Flue Gas</b> .....1</p> <p><b>Fluid Bed Technology</b>.....125</p> <p><b>Fuels</b> synthetic .....39, 65</p> <p><b>Furnaces</b> .....94</p>	<p><b>G</b></p> <p><b>Gas</b> ammonia .....187 flue .....1, 223</p> <p><b>Granular Activated Carbon</b> 105, 136</p> <p><b>Ground-Level Concentration</b> .....85</p> <p><b>Groundwater</b> .....112, 119, 168, 182</p> <p><b>H</b></p> <p><b>Halogenated Organic</b> <b>Compounds</b> .....43</p> <p><b>Hazardous Organics</b> .....171</p> <p><b>Hazardous Waste</b> .....52 incinerators .....246 solidified .....187</p> <p><b>I</b></p> <p><b>Incinerators</b> hazardous waste.....246</p> <p><b>K</b></p> <p><b>Kinetic Control</b> .....259</p> <p><b>L</b></p> <p><b>Laws</b> .....52, 178</p> <p><b>Lender Risk</b> .....178</p> <p><b>Liquid-Phase Mass Transfer</b> .....203</p> <p><b>Lumped-Parameter Modeling</b> ...105</p> <p><b>M</b></p> <p><b>Maleic Anhydride</b> .....151</p> <p><b>Mathematical Model</b> .....259</p> <p><b>Metals</b> .....269</p> <p><b>Modified Clay</b> .....239</p> <p><b>Multicomponent-Adsorption</b> .....105</p> <p><b>N</b></p> <p><b>Nitric Acid Spill</b> .....212</p> <p><b>Nitrogen Oxide</b> .....78, 223</p> <p><b>O</b></p> <p><b>Oil</b> waste .....61</p> <p><b>Oil Shale</b> .....39 retort water .....252 retort water treatment .....145</p> <p><b>Operating</b> experience .....112 problems .....246</p> <p><b>Organics</b> compounds .....14, 23 hazardous.....171 solutes .....252 solvents.....1 volatile compounds .....112</p> <p><b>Oxidation</b> .....46, 229 butane .....151</p> <p><b>Ozonation</b> .....252</p> <p><b>Ozone</b> .....46, 229</p> <p><b>P</b></p> <p><b>Packed Tower</b> .....119</p> <p><b>Peat</b> .....39</p> <p><b>Pilot</b> .....112</p> <p><b>Plants</b> paper.....100 synthetic fuel.....39, 65</p>	<p><b>Pollution</b> .....217</p> <p><b>Process</b> simulation .....1 sludge destruction .....56</p> <p><b>R</b></p> <p><b>Radiation</b> .....229</p> <p><b>Recovery Furnaces</b> .....94</p> <p><b>Recovery Systems</b> groundwater .....182</p> <p><b>Research</b> .....217</p> <p><b>Retort Water</b> .....145, 252</p> <p><b>Risk Management</b> .....20</p> <p><b>S</b></p> <p><b>Scale-up</b> .....112</p> <p><b>Scrubbing</b> wet .....94</p> <p><b>Site Assessments</b> .....178</p> <p><b>Sludge</b> destruction.....56 reuse potential .....165 wastewater .....269</p> <p><b>Solvents</b> organic .....1 recovery and reuse .....161</p> <p><b>Sorption</b> .....239</p> <p><b>Sulfur</b> emissions .....65</p> <p><b>Sulfur Dioxide</b> .....223</p> <p><b>Surface Impoundments</b> .....203</p> <p><b>Survey</b> .....217</p> <p><b>Synthetic Fuels</b> .....39 plant .....65</p> <p><b>T</b></p> <p><b>Thermal Regeneration</b>.....136</p> <p><b>Trace Levels</b> .....239</p> <p><b>Transport</b> ammonia gas .....187</p> <p><b>Treatment</b> contaminated groundwater...168 oil-shale retort water .....145 returned condensate.....100 wastewater .....22, 26, 33, 105</p> <p><b>Trichlorethylene</b> .....119</p> <p><b>U</b></p> <p><b>Ultraviolet</b> irradiation .....252 radiation .....229</p> <p><b>V</b></p> <p><b>Velocity Enhancement</b> .....259</p> <p><b>Volatile Emissions</b> .....141</p> <p><b>Volatile Organic Air Emissions</b>...161</p> <p><b>VOC (Volatile Organic Compound)</b> air emissions .....161 removal efficiency .....14</p> <p><b>Volatile Organic Emissions</b> .....199</p> <p><b>W</b></p> <p><b>Waste Materials</b> .....125</p>
---	--	--

Waste Oil .....	61	industrial.....	22, 46	Water .....	239
Wastewater		oxidation of hazardous		retort .....	145, 252
coal-conversion .....	105	organics .....	171	Wet Air Oxidation.....	171
gasifier .....	33	sludge .....	269	Wet Scrubbing .....	94
H-coal process .....	26	treatment system .....	39	Wise Program.....	155

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