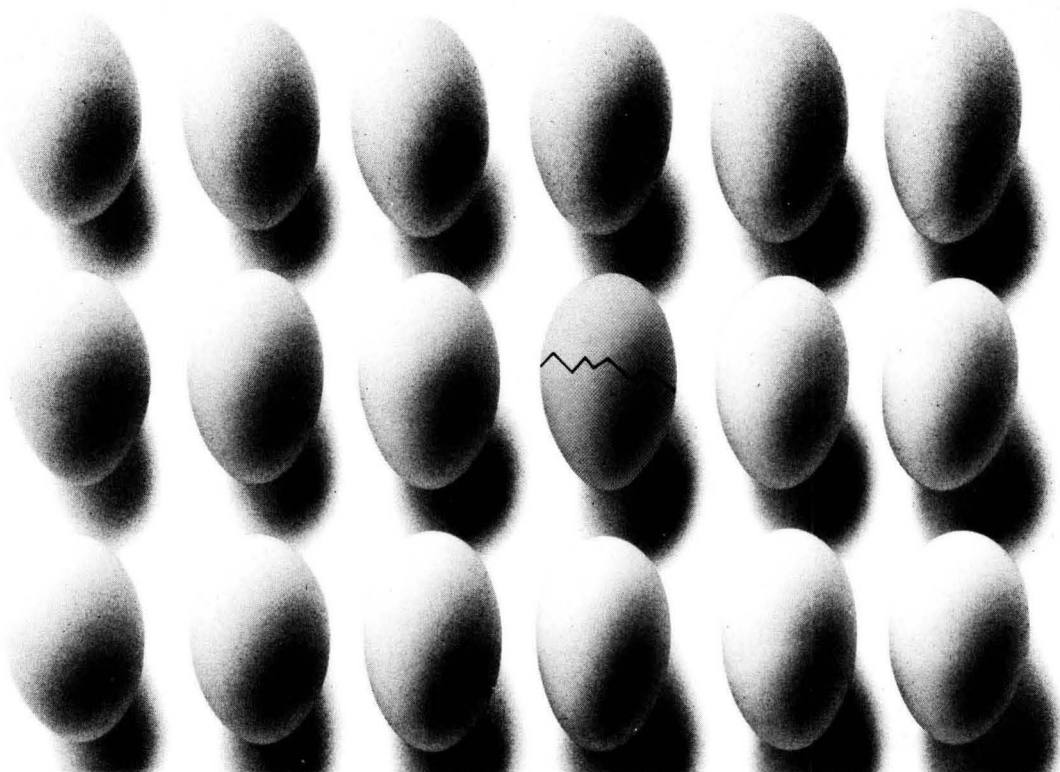


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Cover: Pocket-size monitor designed to protect workers in waste water treatment plants against exposures to hydrogen sulfide.

Photo courtesy of MDA Scientific Inc., Lincolnshire, IL.

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1988 HAZARDOUS MATERIAL SPILLS CONFERENCE

Prevention — Preparedness — Response

**PALMER HOUSE
CHICAGO, IL
MAY 16-19, 1988**

The 1988 Hazardous Material Spills Conference is the ninth in a series of national conferences held biennially on the prevention of, preparedness for, and response to accidental hazardous substance releases. It is the only national conference jointly sponsored by the National Response Team and the American Institute of Chemical Engineers.

Comprised of 14 Federal agencies, the National Response Team has major responsibility in environmental, transportation, emergency management, worker safety, and public health areas. It is the national body responsible for coordinating Federal planning, preparedness, and response actions related to oil discharges and hazardous substance releases.

AIChE is the major technical society for over 50,000 chemical engineers and will be co-sponsoring the Conference for the first time in 1988.

As the leading forum on hazardous material emergencies, the Conference will bring together foremost experts in the field representing government, industry, and academics to present the latest information and research available. This is a unique opportunity to share information about and discuss the latest legislative, regulatory, program, and technology developments in the field. Some of the topics to be addressed during technical presentations include:

- | | | | |
|----------------------|-----------------------------------|--|--------------------------|
| • Hazard Analysis | • Emergency Planning | • Safety Practices | • Design Considerations |
| • Risk Analysis | • Disposal Techniques | • Dispersion Modeling | • Sampling and Detection |
| • Risk Communication | • Clean Up Operations | • Government Programs, Regulations and Standards | • Training |
| | • Alternative Response Technology | • Management Practices | • SARA Title III |
| | • Community Right-to-Know | | |

In addition, an Exposition of industry products and services will be held in conjunction with the Conference.

(DETACH HERE)

Please join us at the Conference. Return this to: AIChE Meetings Department, 345 East 47th Street, New York, NY 10017, USA, or call (212) 705-7325 for further information.

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Environmental Engineering: New Challenges for the Future

Robert L. Irvine

Paul Busch, president-elect of the American Academy of Environmental Engineers, recently noted that the entire environmental field has a major manpower shortage [1]. In 1980 there were approximately 10,000 environmental engineers; 16,000 were needed. In way of contrast, a National Science Foundation survey of science and engineering personnel projected that there would be shortage of only computer specialists and aeronautical/astronautical engineers by 1987 [2]. The question clearly is one of distribution. Scientists and engineers are not being drawn to the environmental field. The social milieu has changed. Earth day has been forgotten. But the problem goes beyond that. Historically, our best high school students have been attracted by the "clean", ostensibly glamorous, high-tech research programs provided by the space industry, the electronics revolution, and astrophysics. Today new developments in superconductivity, computer science, and genetic engineering capture the imagination of our brightest high school and undergraduate students. Clearly, environmental research must be presented as an exciting field in need of sophisticated attention.

New advances in environmental technology must come from mathematicians who can develop algorithms which take advantage of new computer architecture; from microbiologists who can manipulate genetic transfer in mixed cultures to maximize the rate of destruction of hazardous organics; from chemists who can define the reaction mechanisms and kinetics of radicals produced and destroyed by radiolysis and photolysis; and from engineers who can work with scientists to develop innovative technologies for application. Many undergraduates in science and engineering who see pollution control problems from this perspective will choose environmental research as their field of specialization. Their choice is not between sewage and gene manipulation in medical research or between dumps and star wars. Pollution control is a challenging field of study requiring high-tech attention. Indeed, research directed at the removal of carcinogens from the environment is as challenging and as indispensable as basic cancer research itself. Only when these challenges have been accepted will the best students come our way, hopefully in sufficient number to alleviate our manpower shortages.

1. *Engineering Times*, published by the National Society of Professional Engineers, Vol. 9, No. 12, cover page, December 1987.
2. *Science and Engineering Personnel: A National Overview*, NSF 85-302, Washington, DC, 1985.

Dr. Robert L. Irvine is Director of the University of Notre Dame's Center for Bioengineering and Pollution Control and Professor of Civil Engineering. He is the current chairman of the Environmental Division of the American Institute of Chemical Engineers and has served as its Water Section Chairman since 1980. Irvine pioneered work on the Sequencing Batch Reactors for municipal, industrial, and hazardous waste application. He has published one hundred ten papers and technical reports and has given one hundred and twenty presentations at local, national, and international meetings.

ห้องสมุดกรมวิทยาศาสตร์บริการ

Hazardous Substance Research Center Established

The Gulf Coast Hazardous Substance Research Center which was recently established under section 118 (1) of SARA is a consortium of eight universities in five gulf coast states. Members are Louisiana State University, Mississippi State University, Texas Engineering Experiment Station/TAMU, The University of Alabama, University of Central Florida, University of Houston, University of Texas-Austin, and Lamar University-Beaumont.

The center has as its charter, research and development on alternate and innovative technology and waste minimization. A subset

of the Center, the four Texas universities, have received \$600,000 per year for the next two years in state funds. Work has begun on a number of projects including studies on biological treatment of hazardous wastes and leachate, recovery for reuse of a process waste stream, hydrogen peroxide—UV treatment of contaminated groundwater and other waste streams, volatile organic losses from land farming operations and waste minimization in the electronics industry. For further information contact Professor William A. Cawley, GCHSRC, Box 10613, Lamar University, Beaumont, TX 77710.

BOOK REVIEWS

A new Book Review section has been added to *Environmental Progress*. Dr. Robert W. Peters is serving as Book Review editor. Bob has left Purdue University to join the technical staff at Argonne National Laboratory and his new address is:

Dr. Robert W. Peters, Ph.D., P.E.
Environmental Systems Engineer
Energy and Environmental Systems Division
Building No. 362-3D
Argonne National Laboratory
Argonne, IL 60439.

Persons wishing to review a particular book in the environmental field should contact Bob at the above address specifying which book they wish to review.

Hazardous Waste Incineration Services

Phillips Petroleum Company and United Engineers and Constructors Inc., through subsidiaries, have formed a new company to provide hazardous waste incineration services to industry and government.

The company, Incinatrol Inc., will design and build waste incineration facilities based on technology developed at the Phillips Research Center in Bartlesville, OK. Incinatrol's goal is to develop a leadership position in this rapidly emerging industry.

Depending on customer needs, Incinatrol will design and construct hazardous waste incineration facilities for customers, own and operate facilities or operate and provide maintenance for customer-owned facilities.

The company will also provide support services including facility permitting, hazardous waste analysis, manifesting, storage, trial burn and training, as well as related environmental consulting services.

For more information contact Dan Harrison at Phillips Petroleum Company, Bartlesville, OK 74004 (918) 661-5204, or George Bukota, G & A Communications, 49 W. 45th St., New York, NY 10036, (212) 221-2267.

AIChE 1988 Publications Catalog

For a complete listing of all process control titles available from AIChE, consult our 1988 Publications Catalog. If you have not received your copy, send your request to: AIChE Marketing Dept., 345 East 47 St., New York, N.Y. 10017.

Book Reviews

Hazardous Waste Management Engineering by Edward J. Martin and James H. Johnson, Jr., Van Nostrand Reinhold Publishing Co., New York, N.Y. 1987, 520 pages, U.S. List Price: \$67.95.

To play an effective role in hazardous waste management, today's engineers must have a good understanding of the technical, regulatory, economic, institutional, permitting, and public policy issues. In this book, the editors assembled the work of knowledgeable authors having first hand experience in the area of hazardous waste management. The focus of attention centers on the areas of waste destruction, toxicity reduction, and waste minimization.

Chapter one provides an introduction to the area of hazardous waste and chemical substances in terms of a statutory and regulatory review. Two objectives, control and disposal, are discussed. Exposure and risk assessment are addressed in chapter two. These are viewed in terms of the following processes: defining source terms, transport and transformation analyses, locating receptors and defining dose, health effects projection, evaluating risk acceptability, identifying control options, recomputing exposure levels, and monitoring results.

The state-of-the-art chemical, physical, and biological treatment of hazardous wastes are discussed in chapter three. Chapter four describes incineration of hazardous wastes in terms of incineration design principles, types of incinerators, air pollution control systems, rotary kilns, and ocean incineration. The storage of hazardous wastes in

terms of locating storage facilities, sizing, designing, permitting, operating and closure of these facilities are described in chapter five. Chapter six discusses the land disposal (landfills and land treatment) of hazardous waste while chapter seven is concerned with hazardous waste leachate management. The final chapter provides very useful, practical approaches pertaining to the siting process. The authors describe the approval process for the siting of the facility. Considerable data and applications are described throughout the text.

Engineers involved in the field of hazardous waste, such as, environmental, chemical, and civil engineers must have the ability to analyze the various alternatives for hazardous waste treatment and management. This text is a welcome addition to the technical literature. The book will be especially useful to hazardous waste environmental engineers, hazardous waste managers, industrial waste managers, and regulatory personnel.

Robert W. Peters
Argonne National Laboratory,
Argonne, IL 60439

Mobil Waste Processing Systems and Treatment Technologies by W. Glynn, C. Baker, A. LoRoe and A. Quaglieri, Noyes Data Corporation, Park Ridge, N. J., 1987, 136 pages, U.S. List Price: \$36.00

This book summarizes mobile treatment technologies that could be applicable to the clean-up of aban-

doned hazardous waste sites. It may be useful to policy planners in assessing the alternatives associated with land disposal of hazardous waste. The qualitative approach of this book limits its usefulness for design of actual site clean-up. It could, however, be used by engineers as an overview for performing preliminary technology assessment at superfund sites.

The first chapter is an introduction that provides a preliminary screening of potential mobile technologies. This qualitative summary could be helpful in beginning the treatment screening selection process. Thermal treatment processes that might be applicable to site clean-up are discussed in the second chapter. The emphasis in this, and subsequent chapters is on treatment processes, rather than on the complexities of a mobile system.

Immobilization processes that could be suitable for on-site clean-up is described in chapter three. This is followed by chemical treatment technologies in chapter four. Physical and biological treatment are discussed in chapters five and six respectively. The Appendix contains a listing of names and addresses of firms in the mobile hazardous waste treatment business.

While the objective of this book is a worthwhile endeavor, the information is often superficial and incomplete. The book will be of little use to anyone who desires a comprehensive understanding of mobile treatment technologies for hazardous waste site clean-up.

Charles A. Wentz
Argonne National Laboratory
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Washington Environmental Newsletter

Clean Air Act: As part of the reauthorization of the Clean Air Act, an Air Toxics Bill is now under consideration by the US Senate Public Works and Environmental Committee. The bill includes a section on preventing sudden and catastrophic releases of pollutants. Specifically, the bill and amendments include requirements for:

- 1) EPA to publish a list of 55 chemicals specified by the Senate (derived from the SARA 302 list and the proposed NJ Catastrophe Regulations)
- 2) All facilities having one or more of these chemicals on site, in quantities greater than the threshold quantity, to conduct a detailed hazard assessment, and
- 3) An independent chemical safety investigations board to be established whose duties include investigating chemical accidents and recommending to EPA new regulations and orders among other activities.

SARA Section 305 Report to Congress (Prevention): EPA has submitted the "Section 305 Interim Report of Title III—Review of Emergency Systems," to Congress. The report explains the scope and approach of EPA's review of emergency systems and provides a preliminary overview of the state of the art in available technologies to monitor, detect, prevent and provide public alert of accidental releases. EPA distributed a survey questionnaire to over 500 facilities that produce, use or store any of the 21 chemicals (chosen from the SARA Section 302 (a) list of "extremely hazardous substances." Public officials in communities where these facilities are located received a separate questionnaire which focuses on alerting the public to a release from the facility. Both surveys are in final review before distribution. Based on responses, EPA and FEMA will conduct a small number of on-site visits both at the facility and in the community. On-site visits will be conducted with FEMA, the EPA Regional Offices, other Federal Agencies, and State Emergency Response Commissions. Orientation training for these on-site visits is under development.

Information Management Activities: EPA is undertaking new efforts to support state and local organizations in their Title III activities. EPA will: (1) conduct information management workshops (2) collect, organize and disseminate information concerning data bases, computer systems and other tools applicable to information management for Title III and (3) develop model microcomputer systems for emergency planning, notification and right-to-know provisions of the Act.

Hazardous Materials Spills Conference: AIChE along with representatives from EPA, US Coast Guard, FEMA, OSHA, DOT and the Department of Interior are now planning for the 1988 Hazardous Materials Spills Conference—co-sponsored by AIChE and the National Response Team. The conference will cover hazardous materials response, preparedness and prevention issues and is scheduled for May 16-19 at the Palmer House in Chicago. A small exposition will be held in conjunction with the meeting. Mark your calendars and look for further registration information shortly. The Conference has traditionally been held every two years, but this is the first time that AIChE has been a lead sponsor with the NRT.

For additional information on any of these issues, you may contact Dr. Martin Siegel at AIChE's Washington Office (address appears below).

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

Emergency Planning Considerations for Chemical Plants

Eugene J. Michael, Donald W. Bell, and John W. Wilson

Stone & Webster Engineering Corporation, P.O. Box 2325, Boston, MA
and

Gregg W. McBride

Cambridge Analytical Associates, 1106 Commonwealth Avenue, Boston, MA

Well-developed contingency plans for potential emergencies at chemical plants provide safeguards for the plants and their surrounding communities. The size of the emergency planning zone (EPZ) is first determined by use of mathematical models which estimate the health effects and other consequences of toxic, flammable, and explosive chemical releases to the environment. Emergency response plans and procedures are then developed for the EPZ. Finally, a training program is developed and used to ensure that all emergency response personnel are aware of the actions which they must take in the event of an actual emergency.

INTRODUCTION

Emergency planning requirements for chemical facilities are on the increase, notably those in Title III of the Superfund Amendments and Reauthorization Act (SARA) of 1986. It is important for a facility to identify potential hazards, determine the size of the hazard area, and then develop and maintain emergency plans for dealing with these hazards. Successful emergency planning begins with an understanding of the potential accident being considered. Without vital information on types of occurrences and the corresponding potentially affected areas, the contingency plans may not be perceived as having the capability of protecting the public's health and, therefore, probably will not have the necessary support of the community.

Estimates of both onsite and offsite public health and environmental impacts must be made. Whether it is called an environmental impact analysis or a risk assessment, such a study should determine the magnitude of onsite planning requirements, if offsite contingency planning is necessary, and if so, how extensive that planning must be.

Contingency planning for any accident should be structured around three major objectives:

- Understand the type and extent of the potential damage;
- Ensure an orderly and timely decision-making and response process;
- Establish and maintain a high order of preparedness.

From a practical standpoint, the following aspects should be considered and are discussed in turn below:

- Working towards compliance with current and potential federal and state regulations,
- Formulating a planning approach that is acceptable to plant management and, if offsite planning is necessary, to the potentially affected communities and neighboring industries,
- Developing comprehensive yet understandable and workable emergency plans within the constraints of available resources, and
- Establishing and maintaining a cadre of knowl-

edgeable emergency response personnel through the application of well-designed training programs.

REGULATIONS OF HAZARDOUS MATERIALS

A substantial amount of legislation already exists which deals with normal day-to-day plant operations and discharge limitations. Present environmental laws in the United States are as follows:

- RCRA (Resource Conservation and Recovery Act)—Identifies and lists certain hazardous wastes and establishes permit requirements for their treatment, disposal and storage.
- TSCA (Toxic Substance Control Act)—Regulates the introduction of new chemicals into the marketplace.
- OSHA (Occupational Safety and Health Act)—Defines safety and health standards in the working place.
- CAA (Clean Air Act)—Provides a means to regulate certain hazardous air pollutants.
- CWA (Clean Water Act)—Limits releases of toxic chemicals into water supplies.
- SDWA (Safe Drinking Water Act)—Establishes drinking water standards and regulates underground water injection.
- CERCLA (Comprehensive Environmental Response, Compensation and Liability Act of 1980)—Commonly known as "Superfund," which originally provided for cleanup of abandoned, hazardous waste disposal sites.
- SARA (Superfund Amendments and Reauthorization Act of 1986)—Revises and extends the authorities established under CERCLA.

Title III of SARA, also known as the "Emergency Planning and Community Right-to-Know Act of 1986," is a free-standing title within SARA and, thus, is separate from, though closely related to, CERCLA. The authorities and requirements created by Title III, however, will be largely incorporated into the existing National Contingency Plan, established under Section 105 of CERCLA. Title III is intended to encourage and support emergency planning efforts at the state and local level, and to provide

TABLE 1. DEADLINE SCHEDULE FOR SARA TITLE III—EMERGENCY PLANNING AND COMMUNITY RIGHT-TO-KNOW ACT OF 1986

1986	
OCT 17	President signs into law.
NOV 17	EPA: (1) Published list of extremely hazardous substances w/threshold amounts. (2) Initiates a review of emergency systems for monitoring, detecting and preventing releases of extremely hazardous substances.
1987	
MAR 17	National Response team publishes guidance documents for preparation and implementation of emergency plans.
APR 17	State emergency response commissions (ERCs) are appointed by respective governors.
MAY 17	EPA reports interim findings to Congress on review of emergency systems for monitoring, detecting and preventing releases of extremely hazardous substances. Facilities with more than threshold amount of any extremely hazardous substance must notify state ERC which in turn notifies EPA.
JUL 17	State emergency planning districts are established by state ERC.
AUG 17	An emergency planning (EP) committee is appointed by state ERC for each district.
SEP 17	Each facility appoints an emergency coordinator to participate in the local emergency planning process (ERC notified).
OCT 17	Each facility must submit material safety data sheets (MSDS) or list of MSDS chemicals to district EP committee, state ERC and local fire department.
1988	
MAR 1	First annual hazardous chemical inventory forms are due from each facility.
APR 17	EPA issues final report on review of emergency systems for monitoring, detecting and preventing releases of extremely hazardous substances.
JUL 1	First annual toxic chemical release forms are due from each facility.
OCT 17	Emergency Plan is completed for each district.

residents and local governments with information concerning potential chemical hazards present in their communities. Table 1 presents a timeline schedule of the major deadlines of Title III from its passage on October 17, 1986, until the required completion of local emergency plans on October 17, 1988.

Some states (e.g., New Jersey and Illinois) are becoming involved in contingency planning by setting their own regulations. In January 1986, New Jersey enacted the Toxic Catastrophe Prevention Act, also known as the Baer Bill. Any facility operating in New Jersey and handling certain toxic substances must register with the New Jersey Department of Environmental Protection, perform an audit of plant operations, and implement procedures to minimize accident risks. Administrative procedures, enforcement policies, and compliance requirements are thoroughly spelled out in this legislation.

Illinois enacted the Chemical Safety Act in 1985. Its purpose is "to establish an orderly system to assure that responsible parties are adequately prepared to respond to the release of chemical substances into the environment and to improve the ability of state and local authorities to respond to such releases." Written Chemical Safety Contingency Plans had to be in place by July 1, 1986, with copies provided to the local emergency response agencies named in each plan. Regulations specify the coordination between business and these agencies.

FORMULATING AN ACCEPTABLE PLANNING APPROACH

Perhaps the most challenging aspect of any emergency planning project is the coordination effort required to bring industry, government, and private organizations together for the purpose of developing a mutually acceptable solution to a perceived problem. The goal of coordination is to obtain an understanding, commitment, and working relationship prior to and during the development of the emergency plan and to maintain this level of cooperation should an actual emergency response become necessary.

The coordination effort will typically include representatives of corporate and plant management and could include those from neighboring plants. It may also involve community, state, federal, and private agencies. It is in the interest of every chemical plant operator to be thoroughly prepared to answer numerous difficult questions during the planning process, foremost of which is:

"How big will the impact be if there is an accident at this plant?"

Environmental Impact Analysis

One of the first steps in any emergency planning project is to define the Emergency Planning Zone (EPZ), the area for which emergency planning is required. To determine the size of the EPZ, it is necessary to evaluate the consequences of a potential spill or release of toxic material that can contaminate the air, surface water, or groundwater. These consequence evaluations are made with the aid of computerized dispersion models that predict the flow path, travel time, and concentration of the pollutants. These same computer models often can be used for accident assessment purposes during an emergency and also for training purposes once the emergency plans have been developed. An evaluation and assessment of several computer models designed for use in emergency response and planning was recently performed for the Chemical Manufacturers Association (CMA) [1].

It is helpful to perform preliminary hazard evaluations prior to the use of elaborate computer models. An example of this approach is a graphical screening method presented in the Environmental Protection Agency's (EPA's) Chemical Emergency Preparedness Program (CEPP) interim guidance document [2]. The identification of plant hazards is useful at all stages in the life of the plant. Investigations performed in the research and development stage may lead to a substitution of less toxic materials. Those performed during the design stages can lead to reduced holdup of process fluids, immediate use of intermediate hazardous products, implementation of better safety systems, and/or better defined procedures for more efficient maintenance to help reduce the probability of an undesirable event. Better safety systems and/or better defined procedures also result from hazard investigations done during the operational stage. Hazard identification studies should not overlook accidents arising from natural events such as hurricanes and earthquakes. Five common screening methods to locate potential or existing hazards within a plant are as follows:

Checklists: Checklists are used for identifying deviations from good engineering practices and standards through a series of preset questions addressed while inspecting the plant's equipment and facilities.

Safety Audits: Similar to the checklist approach, safety audits also extend into the maintenance and operation of the plant as opposed to only the examination of hardware.

What-if Analysis: This screening method examines and reviews the consequences of unexpected events or deviations from design, construction, or proper operation and maintenance.

Failure Modes and Effects Analysis (FMEA)/Failure Modes, Effects and Criticality Analysis (FMECA): FMEA is a tabulation of plant hardware failures and how these failures affect the plant or its systems. When each failure is given a ranking as to how critical the consequence would be, then the method is called FMECA.

Hazard and Operability Study (HAZOP): The most structured approach to hazard identification, HAZOP requires specialists from various disciplines to work together to ascertain how the operation of a plant can vary from the intent of the design.

Generally, releases to groundwater or surface water are of immediate concern to human health only if drinking water or irrigation of food crops is involved. The pathway of liquids to man is usually well defined and potentially contaminated water supplies can be isolated at readily identified locations. The extent of the planning zone is easily established by identifying all water users who have intakes that may be subject to unacceptable contamination levels from a postulated liquid release.

Airborne emissions, however, are not as confined; they constitute the pathway to man with the greatest possible consequences. The acute human health consequences from a release of toxic or flammable gases can potentially affect many people both onsite and offsite.

The potential effects on plant personnel, nearby residents, and plant and residential properties from an accidental atmospheric release of a hazardous chemical can be summarized as follows:

- Toxic concentrations of hazardous chemicals which can compromise human health.
- Overpressure resulting from immediate or delayed ignition of flammable vapors.
- Thermal radiation effects resulting from chemically initiated fires.

The various analytical techniques described below are routinely used to quantify these potential effects:

Toxic Concentrations: Specialized atmospheric dispersion models are used to evaluate both the outdoor and indoor concentrations of those hazardous and toxic chemicals (including simple asphyxiants) which have the potential to endanger human health. Toxic vapor concentrations and total exposure are calculated as a function of downwind distance, quantity of the chemical released, and meteorological conditions (wind speed/direction, temperature, stability). Indoor concentrations and exposures are also computed based on the time history of outdoor concentrations, ventilation rate, and room volume. The results of these calculations are compared with the most recently published human toxicological data to determine onsite and offsite areas of concern.

Use of these modeling techniques under various accident scenarios and meteorological conditions can assist in the identification of the maximum extent of each potentially toxic plume. In addition, for various potentially flammable chemicals, zones of flammability can be determined by comparative analysis of the predicted concentrations with both their upper and lower flammability limits. Plume concentrations within these flammability limits are capable of ignition and subsequent detonation or deflagration.

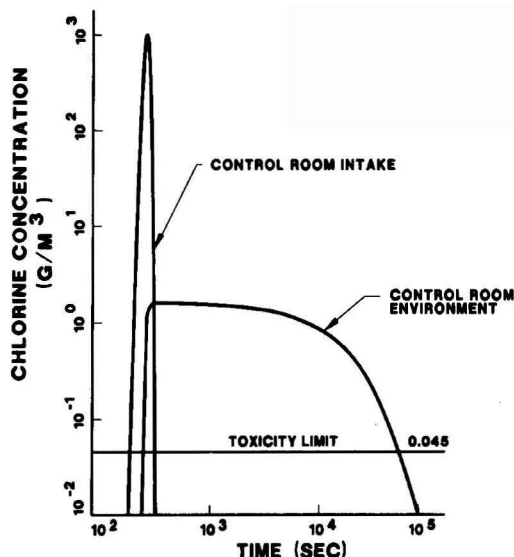


Figure 1. Toxic concentration time-behavior.

Overpressures: Overpressure effects of explosions are determined as a function of downwind distance and meteorological conditions, and are used to assess potential personnel and/or property damage resulting from accidental immediate or delayed ignitions of vapor clouds.

Thermal radiation: Thermal radiation flux calculating techniques are used to determine the extent of thermal radiation effects of a chemical fire. This impact assessment is accomplished by comparing the calculated thermal radiation flux levels with those known to affect personnel or property.

These techniques serve to define the extent of the potential impact areas needed for emergency planning. The impact of certain accident conditions on plant personnel and property, as well as on nearby neighbors, depends on the distance from the accident site, the nature of the hazard, and ambient meteorological conditions. A worst-case atmospheric dispersion condition is used to analyze the extreme impact of a given accident condition. This worst-case analysis yields a preliminary, very conservative EPZ for each chemical considered. These EPZ values are used as input to subsequent risk assessment activities and the offsite emergency response plan. Less conservative EPZs are attainable through greater sophistication in the analytical methods applied.

Analysis of the potential impacts of airborne emissions requires input information on several parameters, including the type of hazard (effects to be protected against), local meteorological conditions, local topography, protective plant design features that influence the rate or location of release, and the physical, chemical, and toxicological characteristics of the involved chemicals.

Once this information is obtained, computer models can generate curves which show airborne concentration versus time for an onsite location following an accidental release. Figure 1 shows such a curve for the case of a process control room where personnel operating the facility are working. Chlorine concentrations outside and inside the control room are shown. The differences in concentration reflect the ventilation rate of the air system and the size of the room. Most important on this curve are the two peak concentrations, their duration, and their relationship to the toxic limit. Obviously, protective actions for per-

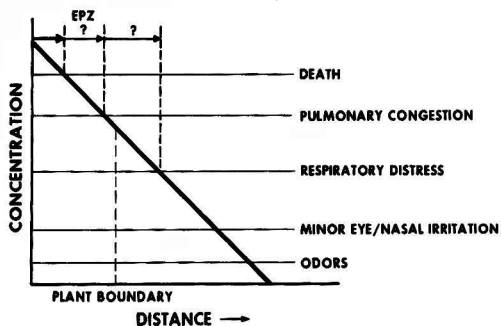


Figure 2. Toxic chemical concentration levels.

sonnel in the control room are warranted in this example. If one were to construct the same type of curve for several distances from the source, plotting maximum concentration versus distance, the curve would appear as a line indicating decreasing concentration with distance (see Figure 2).

To define the impact areas, or EPZ, one of the inputs must be the type of hazard intended to be prevented. Because any given chemical exhibits different health effects at different concentrations, the unacceptable health impact must be selected to determine the extent of the EPZ. The size of the planning area will be directly proportional to the degree of health effect predicted.

The potential acute health effects for a specific chemical can be evaluated by using health assessment criteria (based on experimental or documented experience) or by using health effect levels published as guidelines or regulations. Generally, in a screening analysis, readily available values are appropriate for use. In its CEPP interim guidance document, the EPA suggests using the Immediately Dangerous to Life and Health (IDLH) level published by the National Institute for Occupational Safety and Health (NIOSH). Other levels include the Threshold Limit Value (TLV) published by the American Conference of Governmental Industrial Hygienists (ACGIH) and the OSHA 29CFR 1910 limits.

These values have limitations in applicability because they were established for healthy male worker populations, and sensitive individuals such as the elderly, children, or people with pre-existing health problems are not taken into account. However, these values are often the most readily available for a screening analysis of potential impacts. TLV or OSHA levels tend to be conservative in that they were designed to protect against effects for continuous workplace exposure rather than the short-term acute exposures that may occur in chemical plant accidents. The IDLH or the TLV-STEL (short-term exposure limit from ACGIH) are more realistic but are complicated to a greater extent by the "sensitive individual" issue. IDLH levels represent maximum levels to which a healthy worker can be exposed for 30 minutes and escape without suffering irreversible health effects or impairing symptoms. The TLV-STEL is set by ACGIH and is a maximum concentration to which workers can be exposed for up to 15 minutes without suffering irritation, tissue damage, or impaired function. In many cases, when evaluating less common chemicals or intermediates in a process, health effect guidelines are not available and the toxicological literature must be researched. Experimentally derived values such as the LC_{50} (lowest lethal concentration) or LD_{50} (the lowest lethal dose at which 50 percent of the test animals died) can be utilized in the analysis with appropriate safety factors applied.

Emergency Planning Effort

Assuming that appropriate toxic concentrations have been selected and postulated accidents thoroughly analyzed, the EPZ and the extent of the coordination effort are now defined. For the rest of this article, it is assumed that offsite planning is required. However, the elements discussed are equally applicable to onsite plan and procedure development and have been used in many in-plant as well as community emergency response planning projects.

Because cooperation and commitment are essential elements of successful planning, the best results have been observed and obtained when pre-planning meetings have been conducted with the officials of the potentially impacted communities. Items discussed at these meetings should include a brief description of how the plant works and what safety features have been incorporated to prevent accidents. Results of the plant's accident studies illustrating the EPZ should also be presented. It should be stressed to the officials that the goal of the project is to develop emergency plans and procedures that are flexible enough to help the community to respond not only to an emergency at the plant but to any type of natural disaster, such as a tornado or flood. Finally, what the plant desires from the community during the planning effort should be explained. Once the community officials have had a chance to ask their questions and understand the tasks to be accomplished, they become a very real asset in dealing with the public and the press. Conveying early understanding of the basic emergency functions to local officials is vital to the success of the emergency planning effort.

The CMA, recognizing the importance of community involvement in emergency planning, has developed the Community Awareness and Emergency Response (CAER) Program [3]. The CAER program has two related purposes:

- To develop a community outreach program and to provide the public with information on chemicals manufactured or used at local chemical plants.
- To improve local emergency response planning by combining chemical plant emergency plans with other local planning to achieve an integrated community emergency response plan.

The EPA's CEPP interim guidance document [2] contains recommendations intended to help local communities become aware of any acutely toxic chemicals in their area and prepare to respond to any accidental release of such chemicals into the air. This guidance document is recommended for use in conjunction with the Federal Emergency Management Agency's (FEMA's) informally written planning guide and checklist for hazardous materials contingency plans [4]. This document, called FEMA-10, is addressed to civic officials and emphasizes the planning process rather than technical details. It provides help in deciding whether a plan is needed, in identifying who the planners should be and how the process should work, in identifying the types of plans as well as what they may contain, and in evaluating and updating plans once they are developed. FEMA-10 has been jointly revised by EPA and FEMA and will most likely be a major guidance document in connection with the requirements of Title III of SARA. EPA will supplement this with additional technical documents as necessary.

DEVELOPING THE PLANS AND PROCEDURES

The five most important emergency response functions

to consider when developing an emergency plan for any type of accident are: 1) accident assessment, 2) notification and communication, 3) command and coordination, 4) protective actions, and 5) support actions.

Accident assessment includes detecting abnormal conditions, assessing the potential consequences, and immediately taking appropriate measures to mitigate the situation. It also includes any emergency response actions which must be taken to protect the health and safety of plant personnel and the public. Responsibility for accident assessment normally resides with the plant, which is in the best position to accomplish this function. Real-time, environmental-modeling computer programs for atmospheric or liquid chemical releases are often used to rapidly and accurately define actual hazardous areas within the plant and beyond the boundaries of the site. These same computer programs may be the ones used to establish the EPZ in the first place and also to develop data for plan maintenance through training programs, exercises and drills.

Notification and communication includes the physical and administrative means whereby plant operators can rapidly notify plant management, offsite emergency response agencies, and the public. The importance of notification and subsequent communication equipment cannot be overstated. Without adequate communication, an effective emergency response cannot be implemented.

The command and coordination function clearly establishes who is in charge of the emergency response in the plant and in offsite communities. It also delineates the lines of authority and responsibility for implementing the protective action and support response functions. Coordination is as important during plan development as it is during response; however, it is one emergency response function that is too often inadequately addressed or overlooked.

Protective actions are those taken to protect the health and safety of plant personnel and the public. They may include actions taken to reduce or mitigate the release, sheltering, evacuation, control of access to the contaminated area, and control of contaminated food or water.

Support actions include those activities that take place coincident with or subsequent to the implementation of protective actions. Typical support actions include fire fighting, emergency medical treatment, provision of social services at evacuation centers, and law enforcement and crime prevention during an emergency, especially in areas that may have been evacuated.

During the development of an emergency plan, application of a few well-defined concepts will increase the efficiency of emergency response. Accident assessment, notification, and implementation of protective actions are by their nature sequential tasks. For an effective emergency response, the time necessary to implement these three activities must be minimized.

Accident assessment can be markedly improved through definition of preselected action levels which correspond to system or plant conditions outside of normal operating limits. These emergency action levels (EALs) are selected to enhance the plant operator's indication of any potential or actual problem(s) in advance of any release of toxic substance. Where feasible, EALs should be integrated into the plant's emergency operations procedures and used to trigger early warning to company and, if necessary, public officials. EALs are sometimes interchangeably used with incident classifications. To clarify: incident classification refers to the gradation of emergency conditions from small incidents to catastrophic ones; EALs specify the plant parameter values which require particular defined consequent responses. Plant parameters could include pressure or temperature readings

which vary significantly from normal operating levels or set points, activation of gas detection devices, and the sounding of automatic alarms. They are often identified in the course of hazard definition or risk analysis. Their definition should reduce the ambiguity associated with a wait-and-see attitude when a potential problem is suspected.

The time required to alter plant staff or the public can be shortened significantly by the use of public address systems, electronic or mechanical sirens, radios, or automatic telephone dialing systems. For areas with high population densities, sirens provide the most cost-effective approach. Use of existing sirens is economically advantageous if agreements with owners can be obtained. For areas with lower population densities, tone-alert radios (placed in each home) or automatic dialing systems are most cost-effective. There are political and practical drawbacks to each of these options; therefore, selection of the appropriate system should not depend solely on economic considerations.

The protective action which is least amenable to time reduction and for which the time required to complete is the most difficult to determine is the highest level protective action, evacuation. Nevertheless, preliminary determination of evacuation time can provide insight as to the extent to which the other functions of notification and assessment may need to be reduced. Evacuation times can be estimated for varying weather conditions, seasons, and times of day. Through the use of computerized evacuation modeling techniques, the optimum evacuation routing for potential impact areas can be recommended, thus minimizing evacuation time.

Once full understanding of the five basic functions of emergency response planning is achieved by all involved parties, the development of planning and implementation procedures proceeds rapidly. Existing emergency plans and procedures should be integrated to the fullest extent possible.

MAINTAINING A KNOWLEDGEABLE EMERGENCY RESPONSE ORGANIZATION

Last, but by no means least, is the development and conduct of a training program for plant and offsite emergency response personnel. Classroom lectures, demonstrations, and participation in exercises that test the adequacy of the plan are essential to maintenance of a well-prepared cadre of emergency response personnel.

The goals of any training program are to ensure that participants obtain a thorough understanding of their plans and procedures and develop the leadership and communication skills necessary for confident decision-making during stressful situations.

The main elements of a good training program are:

- Development of training program goals
- Identification of target (common) training groups
- Establishment of group-specific, task-oriented training objectives
- Preparation of student training manuals and visual aids.
- Preparation of individual lesson plans, including hands-on experience if applicable
- Establishment of a training schedule
- Evaluation and correction of the training program

A well-developed and coordinated training program is required, particularly for offsite civilian emergency response personnel. Coordination of training programs conducted by corporate, plant, local and possibly state or federal emergency organizations is recommended to avoid a costly duplication of effort. The frequency with which emergency response personnel receive training

will greatly influence their capability to respond during a test or actual emergency.

A good training program provides initial training for all tasks, periodic review training for those who have been given the initial training, and training for new personnel who might be added at any time. One example of the latter occurs when community elections take place: newly elected officials may require special training in their respective roles in the community Emergency Operations Center during a plant emergency and in the use of emergency response equipment (e.g., the radiopager, which certain officials are required to wear as part of the emergency plan notification process).

By far the best training is received from participation in the enactment of mock accident scenarios during drills and exercises. These serve as positive training experiences and also are advantageous for public relations once the appropriate level of training and readiness is achieved. Their purpose is to give people confidence that the emergency plan works and to identify those weak areas that, once corrected, will ensure that properly implemented plans and procedures can adequately protect public health.

There are two major considerations in the preparation and implementation of a successful drill to test the ability of all personnel and resources to respond to a chemical plant emergency: 1) the formation of a competent, knowledgeable, and highly motivated planning and coordination exercise committee; and 2) the development of a scenario that induces drill participants—the “players”—to demonstrate fully their knowledge and capabilities, and that demonstrates the readiness level of the emergency response facilities and equipment.

The following steps should be followed in the preparation for a complete drill (elements of these can be selected for smaller drills):

- Determine exercise date(s), duration, and timing.
- Decide on exercise objectives.
- Develop exercise scenario that tests the objectives.
- Establish dates, times, and locations for critique meetings and include a system for collection, consolidation, and resolution of critique findings.
- Establish controllers' and evaluators' assignments and associated communications networks.
- Establish a readily observable identification scheme for players, controllers, evaluators, observers, and visitors.
- Prepare, print, and distribute exercise manuals.
- Conduct player, controller, and evaluator pre-exercise briefings.
- Set up logistics support (e.g., provide meals).
- Check and prepare emergency response facilities and equipment.

If possible, one full-scale exercise each year with all outside agencies involved in the emergency plan is recommended. The regular work schedules of personnel involved in the exercise should be considered, especially if overtime expenses are a consideration. In addition, realism requires that offsite participants not be pre-positioned before the start of the exercise. However, to maximize training time and to minimize unproductive travel time, use of pre-positioning is allowable unless the scenario's objectives include determining response times and/or demonstrate activation of emergency response facilities. The use of pre-positioning should be kept to a minimum. For state and local governments that depend on volunteer workers to perform a portion of the offsite response, the exercise committee should accommodate the volunteers as much as possible by minimizing the time away from their normal employment. The scenario should be developed so that players are not idle for ex-

tended periods of time during the exercise. Proper planning can fill such potential gaps with satellite drills.

It is also advisable to test small parts of the emergency plan more frequently through tabletop exercises and mini-drills in such important areas as notification and communication. Finally, it should be recognized that training is just a part of emergency plan maintenance; plans must be continually corrected and updated.

SUMMARY AND CONCLUSIONS

Significant financial savings and good public relations for the chemical industry are attainable through the application of sound emergency planning principles. Well-developed contingency planning for potential emergencies provides safeguards for chemical plants and their surrounding communities. Preparedness and concern for health and safety increases public confidence and forestalls overregulation. Federal and state requirements are on the increase, e.g., Title III of SARA includes several emergency planning and notification requirements that will affect many chemical facilities.

The benefits of contingency planning for the sudden release of a toxic or flammable chemical from a chemical facility are the ability to:

- Pre-identify and prioritize the type and extent of potential accidents for the specific facility.
- Prepare for plausible emergencies.
- Enhance the ability to make timely and orderly emergency response decisions.
- Maintain the availability of equipment and trained personnel corresponding to projected response needs.

Each chemical facility has its own particular set of conditions to which environmental considerations and emergency response planning must be adapted; some plants will thus require more analysis and planning than others. However, a complete and effective contingency planning process begins with determining the size of the EPZ. This leads to developing emergency response plans and procedures for that EPZ, and, finally, to continually maintaining those plans and procedures. A well-trained and exercised emergency response organization with adequate facilities and equipment can best maintain readiness for any emergency. It is recommended that plans be developed considering five important emergency response functions: 1) accident assessment, 2) notification and communication, 3) command and coordination, 4) protective actions, and 5) support actions. Any part of a contingency planning program can be adapted to perceived needs, whether large or small, in-house or offsite, from environmental audits and screening studies through full-scale plan development and implementation of pre-planned test scenarios.

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Wastewater Concentration By Seeded Reverse Osmosis: A Field Demonstration in the Electric Power Industry

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Waste minimization is a key objective of power plant water/wastewater management. Even though membrane processes, such as reverse osmosis, have been used for makeup water treatment, their applications to waste minimization have been very limited. Although the field test results for a seeded reverse osmosis (SRO) system were not absolutely conclusive, the SRO system offers some unique features which may enable the utility industry to realize the advantages of membrane separation processes for wastewater concentration without extensive pretreatment and the associated costs.

INTRODUCTION

Due to increasing limits on wastewater discharges and growing competition for fresh makeup water resources, the utility industry is considering new methods for reducing wastewater treatment costs, and for improving recycle/reuse of plant water streams. Seeded Reverse Osmosis (SRO) offers a new approach to achieve these objectives. The Electric Power Research Institute (EPRI) in conjunction with the Resources Conservation Co. (RCC) conducted a field demonstration test to collect pilot scale operating data to determine the feasibility of using an SRO system as a wastewater concentrator at an electric utility installation. The demonstration was performed at the Utah Power & Light 1200 megawatt coal-fired Hunter Station.

TEST OBJECTIVES

The objective of the field demonstration test was to determine the feasibility of using the Seeded Reverse Osmosis process as a wastewater concentration system. The specific objectives were to:

- Demonstrate that high recovery rates could be achieved for two different wastewater streams; cooling tower blowdown and flue gas desulfurization thickener overflow.
- Demonstrate scale-free operation and determine permeate quality by evaluating SRO process operation parameters (TDS, suspended solids levels, and slurry velocities).
- Observe performance of equipment and tubular RO membranes under seeded slurry conditions.

PROCESS DESCRIPTION

Reverse Osmosis (RO) is a well known technology for concentrating wastewater to recover as much as 80% of the original volume as a relatively high quality and reusable product water. A major constraint with conventional RO is the requirement that the solubility limit of any dissolved species must not be exceeded at any point in the system or membrane scaling will occur. To prevent this occurrence, extensive pretreatment systems are required. The costs of operating and maintaining RO plants with associated pretreatment systems have limited its acceptance and use in the electric utility industry.

A new patented process [1], known as Seeded Reverse Osmosis, eliminates the need for extensive pretreatment by introducing seed crystals into the brine to cause preferential precipitation of scaling components to occur on the existing crystal surfaces. Therefore, wastewaters, with dissolved species approaching their solubility limits, can be processed without pretreatment. In addition, a better quality permeate may be achievable with SRO systems versus RO systems because divalent ions are rejected at a higher percentage than monovalent ions. And in conventional RO systems, monovalent ions replace divalent ions during pretreatment, while no such replacement occurs in SRO systems.

Since the seeded slurry is a suspension of seed crystals, the RO module configuration must provide an unobstructed flow path to prevent physical plugging; therefore, tubular modules are used. A minimum velocity must be maintained to keep the slurry in suspension and minimize the concentration polarization layer. During passage along the membrane, permeate will pass through the membrane causing saturated species in solution to become supersaturated and precipitate. The supersaturated species precipitate on the existing crystals suspended in the stream instead of on the membrane wall (Figure 1). A hydrocyclone is used in the reject stream to return the seed crystals to the sump tank, which provides feed to the modules. In the sump tank, further precipitation occurs until the solution is at its saturation level. The seed crystals need to be introduced only at start-up. The only chemical additions to the system are sulfuric acid for pH control, and sodium hypochlorite to prevent bacterial attack.

Initial laboratory testing of the process, using synthetic cooling tower blowdown as feed, was completed in 1982 [2] and a five-element pilot test unit was installed in 1983 to field test a mining operations wastewater stream. The test program accumulated over 8,000 hours of operational experience without any evidence of scale formation. Water recovery ratios achieved were approximately 95% [3]. Hunter Station cooling tower blowdown wastewater chemistry is very similar to that of the mining operations wastewater.

PILOT UNIT DESCRIPTION

A portable SRO pilot unit was used in this test program. A schematic for the 62 Module SRO Test Unit is displayed in Figure 2. The pilot unit consisted of three assemblies or reactions: #1, #2 and #3, each containing type A-2¹ cellulose acetate tubular RO modules in series with associated tanks, pumps, piping, instrumentation, controls, etc. After the initial addition, seed was recycled back into the reaction feed tanks (sumps) by running the reject through hydrocyclones to recover the seed. Each reaction contained a sump to provide residence time for the precipitation of the supersaturated reject brine, and a

boost pump, which adjusted for hydraulic losses and the higher osmotic pressure. Chemical addition was accomplished in the first reaction sump where sulfuric acid was added for pH control and sodium hypochlorite was introduced to prevent biological fouling or attack. The final reject was discharged to the sewer.

During the cooling tower blowdown testing, the pilot unit was reconfigured to evaluate the performance of five different tubular RO membrane formulations. All the modules, types A-1, A-2, B, C, and D, were cellulose acetate but with various membrane formulations and module designs. Modules A-1 and A-2 had the same module design, but different membrane formulations. Module A-2 was the formulation used in the first two phases of testing. The instrumentation needed to control and monitor the system consisted of pressure and temperature gauges, permeate and reject flow meters, permeate and reject conductivity meters, and pH meters on each tank.

TEST APPROACH

In order to demonstrate the SRO system on wastewaters associated with an electrical power generating station, cooling tower blowdown (CTB), and flue gas desulfurization thickener overflow (FGD TOF), were selected for testing. The analyses for the chemical constituents of both raw feed waters are listed in Table 1. Based on these chemistries, it was predicted that the SRO system could recover in excess of 75 percent of the CTB as medium quality permeate which could be recycled back to the plant. The anticipated recovery when treating the FGD TOF was 60 percent with a medium quality permeate. Performance of the system was evaluated primarily using the three key parameters: recovery, rejection, and productivity coefficients. Recovery is the ratio of total permeate flow to raw feed flow into the system.

$$R = (Q/F) \cdot 100 \quad (1)$$

where: R = system recovery
Q = permeate flow rate, and
F = raw feed flow rate.

Rejection governs the quality of the permeate and is the percentage of ionic species not transported through the membrane into the product water.

$$\% \text{ Rejection} = [1 - (2 \cdot \text{TDS}_Q / (\text{TDS}_{in} + \text{TDS}_{out}))] \cdot 100 \quad (2)$$

where: TDS_Q = permeate TDS (mg/l),
 TDS_{in} = stream into modules TDS (mg/l),
 TDS_{out} = stream out of modules TDS (mg/l).

Productivity coefficients identify how much product water was being extracted per surface area of membrane and effective pressure. To obtain the productivity in SI units of $1/(\text{m}^2 \cdot \text{bar} \cdot \text{day})$ multiply K by 591.

$$K = (Q_T \cdot 1440) / (P_{EFF} \cdot A) \quad (3)$$

where: K = productivity (gfd/psi),
 Q_T = temperature corrected permeate flow rate (gpm),
 P_{EFF} = effective pressure (psi), and
A = area of membrane surface per reaction (ft^2).

Test Plan

For both cooling tower blowdown and FGD thickener overflow, the testing was conducted in three steps:

- Initial 2000 ppm sodium chloride (NaCl) baseline test,

¹ The different membrane formulations referred to in this report come from four different manufacturers identified as A, B, C, and D. In the case of manufacturer A, two membrane formulations were tested identified as A-1 and A-2.

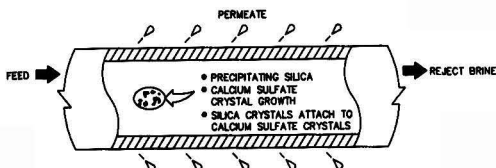


Figure 1. Seeded reverse osmosis concept.

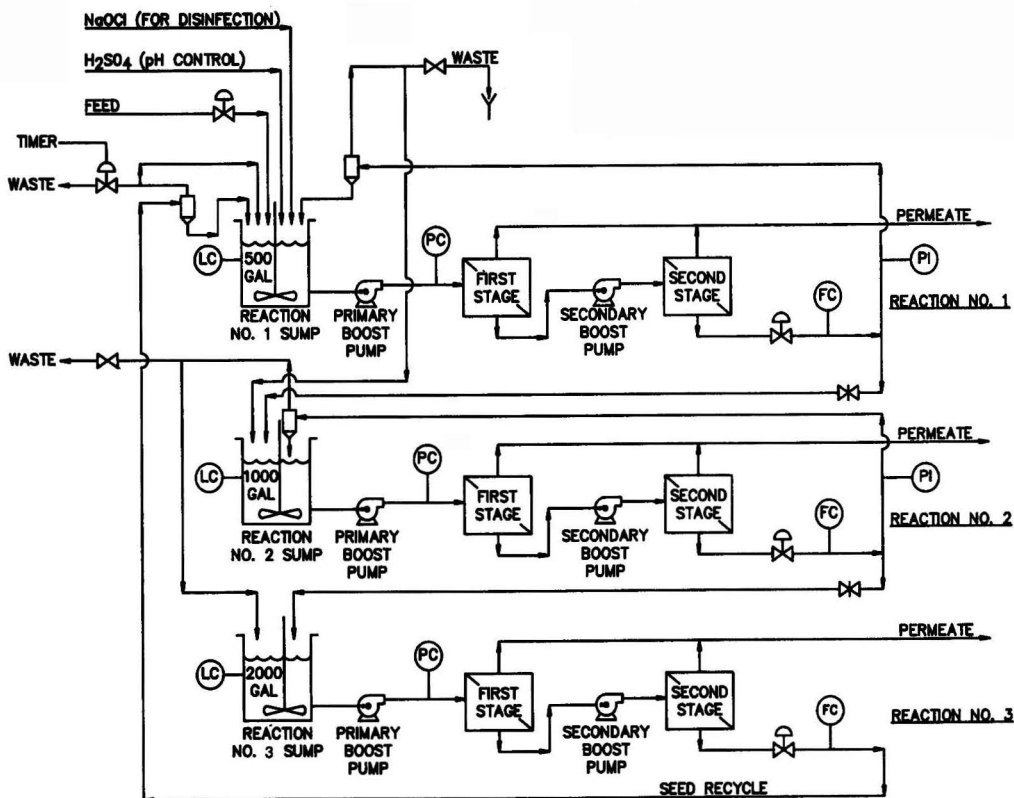


Figure 2. Schematic of test unit for cooling tower blowdown phase.

- Wastewater feed source test, and
- Final NaCl test.

A performance baseline was established by conducting a sodium chloride test under specific operating conditions. This test also provided a means for system check out and is the standard used by most RO manufacturers to evaluate their membranes. During the initial 48-hour NaCl test, data were taken to evaluate pressure drops, membrane productivity, and ionic rejections. The test was operated under total recycle conditions, so all the permeate and reject were recycled back to the feed tank. The expected increase in temperature was controlled using a heat exchanger.

The second step was the processing of the selected wastewater. The initial operating conditions for treating the CTB and FGD TOF are listed in Table 2.

Samples were taken once a day. Sampling discharge valves were located on each sump, and each reaction reject brine line. Samples were also taken at each waste and permeate discharge line and the raw feed line. In addition to daily samples, retention samples were taken for later chemical analysis. Samples of membrane tubes from the modules used in the different tests were taken for both laboratory testing and Scanning Electron Microscopic (SEM) analysis. A sample log of all samples taken, date and time, and location was kept at Hunter Station. Data included: date and time; pressures in and out of each reaction; permeate and reject flow rates; feed, reject, and permeate conductivities; temperatures at each group of modules; sump pH's; Total Dissolved Solids (TDS) of feed, reject, and permeate from each reaction; and Suspended Solids (SS) of feed, reject and waste from each re-

action. These data made monitoring the performance of the test units current throughout the test periods so corrective action could be taken quickly.

TABLE 1. RAW FEED CHEMISTRY FOR CTB & FGD TOF

Constituents		CTB	FGD TOF
Conductivity	(μmho/cm)	4,400	14,900
Calcium	(mg/l)	530	740
Magnesium	(mg/l)	300	1,700
Potassium	(mg/l)	11	33
Sodium	(mg/l)	390	990
Chloride	(mg/l)	160	3,900
Fluoride	(mg/l)	2	39
Nitrate	(mg/l)	1	22
Sulfate	(mg/l)	2,900	4,800
Silica	(mg/l)	29	92
Suspended Solids	(mg/l)	35	67
TDS	(mg/l)	5,000	15,500

TABLE 2. INITIAL OPERATING CONDITIONS

	CTB	FGD TOF
Operating Pressure (psig)	400 (29 bar)	500 (36 bar)
Feed Rate (gpm)	10.7 (41 l/m)	1.5 (6 l/m)
Permeate rate (gpm)	8 (30 l/m)	0.9 (3 l/m)
Feed pH	5-6	5-6
Feed Chlorine (ppm FAC)	0.1 to 1.0	0.1 to 1.0

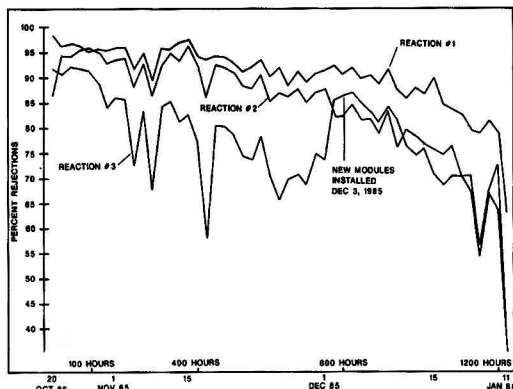


Figure 3. Percent rejections.

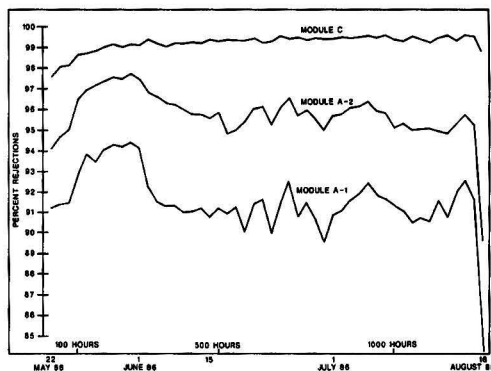


Figure 5. Modules A-1, A-2 & C percent rejections.

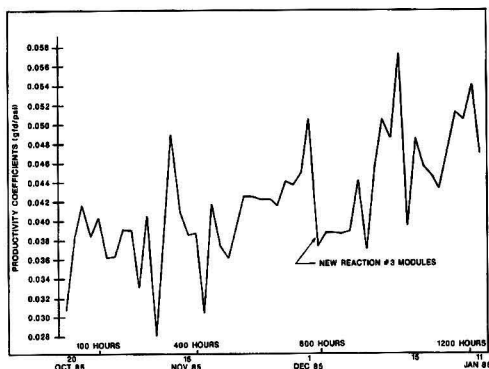


Figure 4. CTBD overall productivity coefficients—Phase I.

Final salt rejection tests were performed at the end of the cooling tower blowdown and FGD thickener overflow tests. The purpose of these tests was to evaluate any differences in productivity coefficients, percent ion rejection, or pressure drop that occurred relative to the initial baseline tests.

DISCUSSION OF RESULTS

Cooling Tower Blowdown Results

The 62 module test unit operated with recoveries of 73 to 81 percent, concentrating the brine approximately 3.7 to 5.3 times without scaling.

The rejections for the first 1200 hours of testing are displayed in Figure 3. These data reveal that the rejection for reaction #3 decreased significantly (7 percent) within the first 300 hours of testing. The increase noted on December 3 is the result of the replacement of some modules, but the subsequent decay was immediate. The other reactions displayed rejection loss, with reaction #2 at a slower rate than reaction #3, and reaction #1 at the slowest rate of decay. This indicated that whatever was destroying membrane quality was in greatest concentration in reaction #3. The overall productivity coefficient was an average of the three reactions and is displayed in Figure 4. The average overall productivity increased from 0.031 to 0.041 gfd/psi (18 to 24 $l/(m^2 \cdot bar \cdot day)$). Typically productivity decreases due to compaction and fouling of membrane and increases with loss of membrane surface.

An on site dye test was performed to indicate where the membranes were degrading. The dye test revealed a loss of membrane quality on every tubelet examined. Scanning Electron Microscope (SEM) examination revealed a large bacteria population, in spite of chlorine addition, and small holes on membrane surfaces along the entire length of the tubelets. The increase in observed productivity is not characteristic of bacterial attack of membranes because bacteria typically attach to membranes and foul them. Another type of bacterial attack occurs when bacterial waste products react with the membrane to destroy it.

During the first 800 hours of operation, the lack of CTB feed made it necessary to add service water to ensure continuous operation. The service water system ties into the ash sluicing system. It was discovered that intermittently the service water was laden with bottom ash particles, which were found in the sump samples. Three pos-

TABLE 3. PERCENT REJECTIONS

Module	Initial	Final	Average	Range**
A1	95.5	82.4	91.8	95.5-89.6%
A2	96.1	90.3	96.1	97.7-95.0%
B1	92.2	94.7	96.8	97.5-93.8%
B2	91.4	93.3	97.5	98.9-94.3%
C1	93.4	98.7	99.1	99.6-98.1%
C2	90.2	*	97.4	97.2-95.0%
C3	95.7	*	98.8	99.2-97.7%
C4	93.4	98.7	99.1	99.5-97.6%
D1	93.0	84.0	92.0	93.9-89.2%

* Testing on these modules was incomplete.

** Low values in range do not include initial or final salt tests rejection values. Most of the low values were from the first day of operation and were not experienced again.

TABLE 4. INDIVIDUAL MODULE PRODUCTIVITY (GFD/PSI)*

Module	Initial	Final	Average	Range**
A1	.040	.043	.047	.043-.052
A2	.038	.026	.037	.035-.044
B1	.045	.040	.044	.040-.048
B2	.042	.038	.042	.037-.050
C1	.048	.039	.044	.039-.050
C2	.043	***	.043	.042-.045
C3	.050	***	.049	.046-.051
C4	.064	.040	.046	.040-.064
D1	.063	.051	.054	.047-.067

* To obtain the productivity in SI units of $l/(m^2\text{-bar}\cdot\text{day})$ multiply K by 591.

** This represents the productivities during operation on CTB feed and does not include initial and final salt rejection values.

*** Testing on these modules was incomplete.

sibilities were suggested to explain the loss in rejection and increase in productivity of the membranes: biological attack, chemical attack, or erosion of the membrane surface. Efforts were directed to determine the cause.

In previous testing, modules furnished by manufacturer A had not exhibited the degradation seen during the first 1200 hours of operation. They had been tested under typical operating conditions using synthetic CTB as feed in the laboratory. The synthetic feed in these tests did not contain any ash. Therefore to determine the affect of bottom ash on these membranes, a synthetic CTB feed with bottom ash added was used to conduct a separate laboratory test under controlled laboratory conditions. Loss of rejection and failure of the membranes occurred within hours.

Samples of used and new A membranes were also examined using a microscope and an SEM. The SEM examination found tiny $0.5\ \mu$ particles embedded in the used membranes. These particles were subsequently determined to be predominantly silica. This was concluded to be the reason for membrane degradation.

The CTB field testing was continued with five different membrane formulations from four RO manufacturers (A, B, C, and D), because the initial 1200 hours of data indicated that manufacturer A's type A-2 membranes were unsuitable for SRO operations. During this additional testing, the pilot unit was operated at a 95 percent recovery and at a minimum operational seed level for the first five weeks and a seed recovery level of approximately 25,000 ppm the last three weeks. A coarse filter was used for the CTB raw feed.

None of the RO modules demonstrated the loss of rejection experienced in the first 1200 hours of operation. This was due to the reduction of ash in the system and the lower seed level maintained. All the modules varied significantly in performance, which was expected. The rejections experienced during the membrane performance evaluation are listed in Table 3. Figure 5 displays the rejections for modules A-1, A-2, and C. Module C had the most consistent rejection, while both modules A-1 and A-2 lost rejection at approximately 300 hours of operation. Module A-1's average rejection stabilized while A-2's average rejection continued to decrease slowly. The final salt test rejections for modules A-1, A-2, and D were unusually low and it is suspected that insufficient circulation of the preservative solution occurred between operation on CTB feed and the final salt rejection test. The productivities varied significantly among the different modules. These are listed in Table 4 and the productivities for modules A-1, A-2, and D support the explanation of insufficient circulation of preservative solution. Figure 6 displays the productivities for modules A-1, A-2, and C. This

indicates that only module A-2 increased in productivity after 500 hours of operation.

Although the A-2 module did not fail at the rate experienced in the first 1200 hours, the drop in rejection in conjunction with the increased productivity indicates a slow failure of the module. The failure was gradual because the particulate and seeded environment, the module experienced in this testing, was better controlled by coarse filtration. The gradual failure of the A-2 module suggests that the A-2 membrane formulation cannot sustain a seeded or particulate environment.

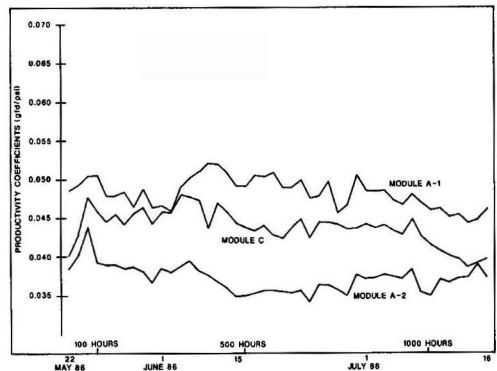


Figure 6. Modules A-1, A-2 & C productivity coefficients (gfd/psi).

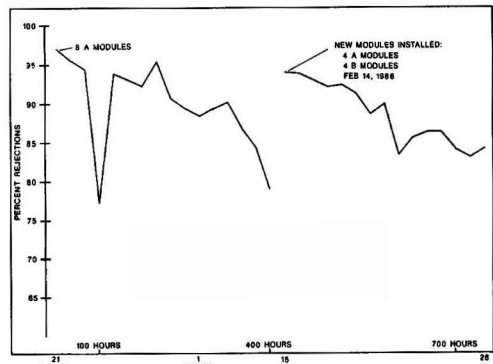


Figure 7. Percent rejections.

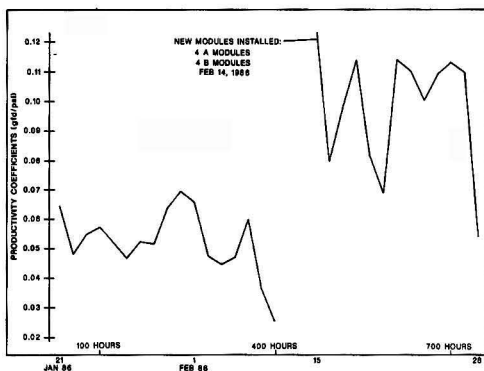


Figure 8. Productivity coefficients.

FGD Thickener Overflow Results

This test started after the problems associated with the earlier cooling tower blowdown test had been experienced. Benefitting from those earlier results, several modifications were made to the pilot unit. Due to the high sulfite level and the concern of the bacterial activity of the FGD TOF raw feed, the raw FGD TOF feed was shock chlorinated to 30 ppm free chlorine and then treated with sodium bisulfite to lower the chlorine level to 1-3 ppm FAC. This shock chlorination eliminated the possibility of bacterial attack being the cause of the loss in rejections and increase in productivity experienced with the earlier CTB testing. Coarse filters were added to the raw feed supply stream to minimize the introduction of ash into the system. Due to the high feed TDS of the FGD TOF, it was expected that lower recoveries would be experienced. The overall system recovery achieved was 60 percent and the system operated scale free.

Initial testing started using the A-2 modules. Within 340 hours of operation, the rejections dropped steadily from 95 percent initially to 78 percent. On February 13, 1986, four of manufacturer A's modules were replaced with manufacturer B's modules. To maintain a baseline for comparing the different modules, four new A modules were also installed. Within the next 340 hours of operation, the rejections dropped steadily from an initial 94 percent to 86 percent, but only the A modules failed. A survey of individual module permeate conductivity indi-

cated that B modules maintained their permeate quality while A-2 modules escalated to more than 3.5 times their initial conductivities. The rejections are shown in Figure 7 and, as noted, the rejections increased with the replacement of the modules.

CONCLUSIONS

The field testing at Utah Power & Light, Hunter Station demonstrated that Seeded Reverse Osmosis (SRO) is a technically viable approach for concentrating typical power plant wastewaters, such as cooling tower blowdown and thickener overflow from the flue gas desulfurization system. During the entire operation of the SRO system at Hunter Station, the pilot unit operated scale free and the hypochlorite addition system prevented bacterial fouling of the membranes.

The selection of RO modules is critical for the successful operation of the SRO system. Variations in productivities and rejections demonstrate the significant differences among manufacturers RO modules. The performance of the A modules throughout the testing suggests, that some membrane formulations cannot maintain their integrity in the presence of abrasive foreign solid particles, and may require removal of these particles in order to consistently perform well.

The performance of the A-2 modules indicate that this particular RO membrane cannot effectively operate in an SRO system due to the erosion of the membrane surface in the seeded and particulate environment.

The issue of SRO economics compared to other commercially proven wastewater concentration methods still must be addressed. An economic evaluation is being prepared as part of the current EPRI research project (RP2114-7). The results of this field test indicate that SRO is a viable new technology which could enable the electric utility industry to reduce wastewater treatment requirements and improve plant water recycle and reuse.

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In-Situ Bionitrification of the S-3 Ponds

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A process has been developed for removing nitrates and heavy metals from open ponds. Four ponds were treated using the developed process. The process steps involved neutralization of the ponds, followed by biological denitrification. The nitrate ions were reduced from 40,000 mg/L to <50 mg/L at an average denitrification decrease rate of 300 mg/L per day. The denitrified water was then flocculated and filtered to remove solids. The water quality met discharge water chemical limits as well as biological test requirements.

INTRODUCTION

The Oak Ridge Y-12 Plant is owned by the U.S. Department of Energy (DOE) and is operated by Martin Marietta Energy Systems, Inc. The major responsibilities of the plant are (a) producing weapons components and supporting DOE's design laboratories, (b) processing special materials, (c) supporting other DOE Oak Ridge Operations installations, and (d) supporting other government agencies.

Nitrate wastes are produced from liquid-liquid solvent extraction processes used in uranium purification, where nitric acid is a principal reagent. In the past, waste solutions from the extraction processes and other sources were pumped into a series of four unlined surface impoundments, referred to as the S-3 ponds. The ponds had no overflow and evaporation, and percolation prevented the liquid from reaching overflow levels. In 1983, it was agreed that all discharge of waste material into the ponds would cease, and a proposal for decommissioning the ponds was prepared. It was proposed to carry out extensive testing of *in situ* treatment, leading to the treatment of one of the ponds on a demonstration basis. Techniques developed in the demonstration work were to be used for decommissioning the other three ponds.

LITERATURE REVIEW

Bionitrification has been described as the enzymatic reduction of nitrites, and nitrates by bacteria to nitrogen gas [1]. A large number of microorganisms are capable of denitrifying, including organisms of the genera *Pseudomonas*, *Thiobacillus*, *Micrococcus*, and *Achromobacter*. For denitrification to take place at a rate that may be usable in pollution control processes, various parameters must be within limits suited to the replication of denitrifying bacteria. Various researchers [2, 3] have shown that nitrate reduction is optimum at neutral pH ranges. Temperature is a critical factor in denitrification rates. Mechals *et al.* [2] found that the denitrification rate doubled for a 10°C increase in temperature. Bremmer and Shaw [4] confirmed the above, but noted that the rate increase was

less pronounced at higher temperatures. They also found maximum denitrification to take place at 60°C.

Several organic compounds have been used successfully as carbon sources for denitrification. Methanol is commonly used because of efficiency, availability, and economics. McCarty *et al.* [5] showed that methanol, ethanol, acetone, sugar, and neutralized acetic acid could be used in the denitrification process. Also shown was the fact that neutralized acetic acid solutions were decomposed at a more rapid rate than methanol solutions. Clark *et al.* [6] found that calcium acetate used as a sole carbon source gave very satisfactory bionitrification results.

TABLE 1. INSIDE DRUM-SIZE TESTS

Chemical elements	As taken	Neutralized	After-denitrification
(All elements except pH are in mg/L)			
NO ₃	8300	—	<50
TOC	—	1900	—
pH	2.7	8.5	7.5
Ag	<0.009	<0.009	<0.009
Al	740	3.17	0.19
B	7.7	0.38	1.5
Ba	0.25	1.34	0.006
Be	0.08	<0.005	<0.005
Ca	930	3658	—
Cd	0.27	<0.013	<0.013
Co	0.22	<0.023	0.015
Cr	4.3	0.09	<0.001
Cu	6.2	0.26	0.12
Fe	19.4	0.98	0.09
Mg	137	5.94	15
Mn	4.8	<0.0003	0.031
Mo	0.22	0.13	0.095
Ni	41.6	0.07	0.91
P	6.1	0.28	4.56
Pb	1.1	<0.12	<0.12
Th	0.39	—	<0.005
Ti	<0.02	<0.02	<0.02
Zn	4.3	<0.007	<0.007

Based on the reported results, the Y-12 Plant has consistently used calcium acetate in connection with its biodenitrification processes.

LABORATORY TESTS

The southwest pond at the S-3 ponds was selected for demonstration work. Samples from that pond were subjected in the laboratory to neutralization with calcium hydroxide and acetate ion was added to create a 1.3 to 1 carbon to nitrogen weight ratio. Samples were seeded with sludge taken from an operating continuous-flow bioreactor and 20 mg/L of phosphate were added. These tests were beaker-size and conducted at ambient laboratory temperatures (20°C nominal). After approximately 80 days, bacteria were decomposing nitrates at an approximate rate of 300 mg/L/day and a total of 120 days were required to complete denitrification. The beaker tests showed that neutralization was very effective in inducing the precipitation of a variety of elements, particularly heavy metals. Denitrification proceeded to levels below 50 mg/L, at which point the bioreaction was considered to have been completed.

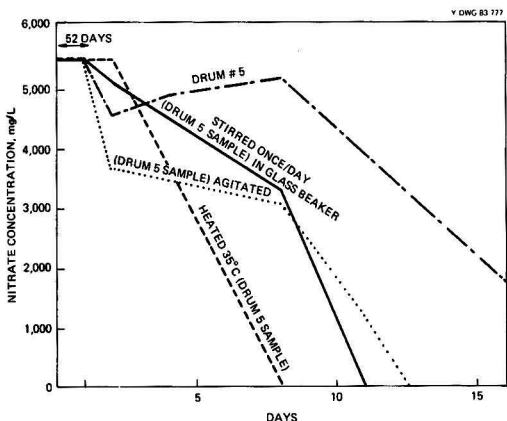


Figure 1. Effect of temperature and agitation on denitrification rate.

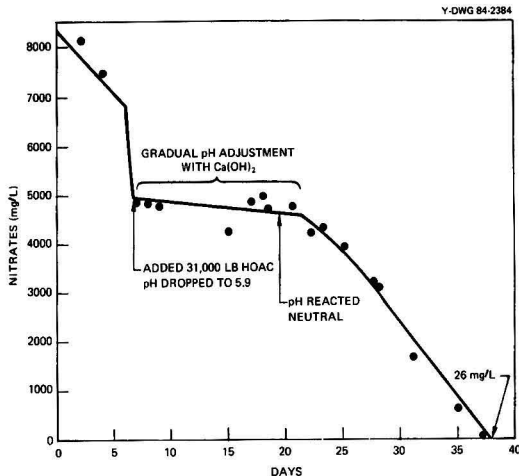


Figure 2. Nitrate concentration, southwest pond.

During the beaker tests, field tests using 0.21 m³ (55 gallon) drums were also undertaken. Five drums were used, four being left outside during winter and spring months and one kept inside a heated building. As in the beaker tests, most of the heavy metal ions were precipitated after neutralization using calcium hydroxide. The outside drums showed little bacterial growth and no denitrification was evident after a 100 day period during the winter months. As expected, cold ambient conditions have a very negative effect on biological denitrification.

The fifth drum, kept at a temperature of approximately 27°C, required 60 days to acclimate and an additional 40 days to denitrify. Comparing the data from the beaker tests and the indoor drum test, the denitrification rate was found to be slower in the drum test, with the maximum denitrification rate being a nominal 200 mg/L per day. Results of the inside drum test are given in Table 1.

Three beaker tests were conducted with liquid taken from the indoor drum test at the start of denitrification. One beaker was continuously stirred, a second one was thermostatically heated at 35°C, and the third was stirred once a day for 30 s. As can be seen from Figure 1, heating and agitation, even as slight as 30 s/day, was sufficient to accelerate the denitrification to nitrate reduction rates greater than 600 mg/L per day. The continuously stirred beaker took slightly longer to denitrify than the slightly stirred beaker. In all cases, it was observed that the bacteria formed on the precipitate and produced large flocs that rapidly settled. The stirring action appeared to help release gas formed within the solids. Experiments indicated that the biological activity in the biodenitrifying reactors is inhibited at acid pH ranges. Conditions below a pH of 6.8 were found to inhibit activity in stirred solutions. In unstirred solutions, major biological activity ceased, although a small amount of gas evolution was noted indicating that local areas of denitrification were occurring. It is theorized that this inhibitory effect is related to the solubilities of the various heavy metals previously precipitated rather than to a direct effect of the pH upon the active biological mass.

TABLE 2. WATER QUALITY DATA, SOUTHWEST POND

Chemical elements	Before neutralization	After neutralization and denitrification
(All elements are in mg/L)		
NO ₃	—	47
TOC	260	100
U	35	2.6
Ag	<0.009	<0.009
Al	740	0.45
B	7.7	3
Ba	0.25	<0.2
Be	0.08	<0.005
Ca	930	—
Cd	0.27	<0.007
Co	0.22	0.009
Cr	4.3	0.003
Cu	6.2	0.078
Fe	19.4	0.96
Mg	137	47
Mn	4.8	0.013
Mo	0.22	0.16
Ni	41.6	0.32
P	6.1	1.41
Pb	1.1	<0.015
Th	0.39	<0.04
Ti	<0.02	<0.02
Zn	4.3	0.008

In Situ Treatment Test

The southwest pond was chosen for a pilot test of the *in situ* treatment process. The chemical characteristics of the water in the pond are given in Table 1. The initial pond pH was 2.7 and the average nitrate concentration was given as 8,300 mg/L. The mixing system consisted of five valved intakes located along the north side of the pond. The intakes were submerged approximately five feet and were provided with strainers. The flow from this manifold was pumped by two 4,000 L/min pumps through a discharge manifold composed of five outlets located on the west wall. A third pump was located near the southeast corner and was used to recirculate that area of the pond. Neutralization was performed through the addition of finely ground calcium carbonate, sodium hydroxide, and calcium hydroxide. Lime was added through a slurry tank fed by a pump dedicated to that purpose. Other chemicals, such as sodium hydroxide and acetic acid, were added through a 0.5 m drain originally used for liquid addition to the pond. Bionitrification sludge was added directly into the pond as seed.

The primary neutralization reactant used was calcium carbonate. This chemical was added to a pH of approximately 5.0. Several days after the addition of calcium carbonate, acetic acid was added. The pH dropped to 4.0 as a result of the acid addition. Several additional days of mixing showed no change in the pH of the water. Sodium hydroxide as a 50% solution was added to obtain a pH of 6.6. During the bionitrification phase, pH was adjusted using calcium hydroxide.

Unlike laboratory experiments, it was found that bacteria in the ponds acclimated in a short period of time, and signs of active bionitrification were observed within a few days. At the beginning of the biological process, there were 8300 mg/L nitrates and 1600 mg/L total organic carbon (TOC) in the pond, which gave a C:N weight ratio of 0.85. This was lower than desired and, because of shipment delays, the required amount of acetic acid was not introduced until the test was in progress. Figures 2 and 3 represent the nitrate concentration, dissolved oxygen (D.O.), temperature, and pH in the pond during the test. As can be seen, denitrification proceeded at a rapid rate with a concurrent D.O. drop and a temperature rise. A drastic pH drop at day nine was the result of an acetic acid addition. As a result of this drop, bionitrification stopped for approximately two weeks. After a

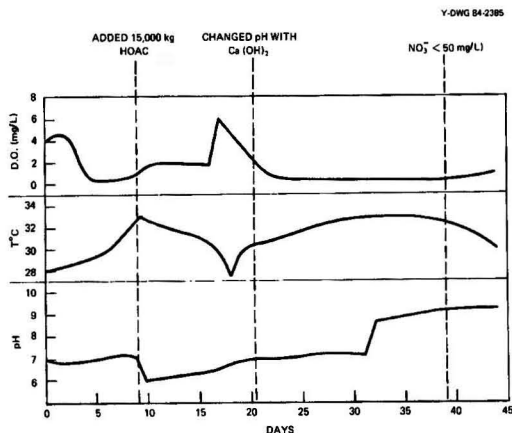


Figure 3. Conditions during bionitrification, southwest pond.

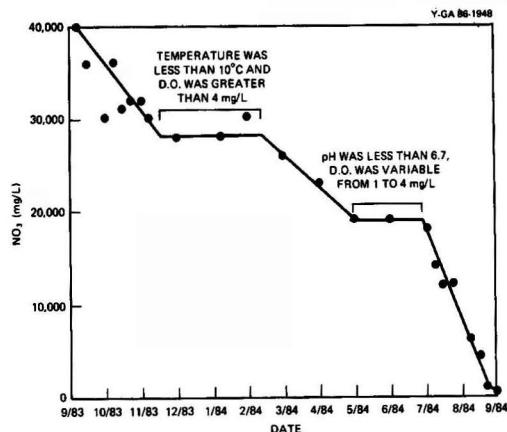


Figure 4. Nitrate concentration, northwest pond.

gradual pH adjustment, the D.O. began to decrease and the temperature increased as denitrification resumed. The rate of denitrification over the final phase was approximately 300 mg/L/day until the nitrate level reached 26 mg/L.

After denitrification, some of the remaining organic carbon was removed by bio-oxidation. After an aerator was installed, organic carbon decreased at a nominal rate of 37 mg/L/day for a period of seven days, after which the TOC level remained stable. At that point, the acetate carbon portion of the remaining TOC was less than 50 mg/L. The TOC that remained, appeared to be in a form not easily metabolized by the microorganisms, and was found to remain present after several additional weeks of aeration. The quality of the water before and after treatment is shown in Table 2. As can be seen from these data, water quality after neutralization and biological treatment was excellent.

NORTHWEST POND TREATMENT

Treatment of the northwest pond was begun in September 1983. The mixing system was moved to this site

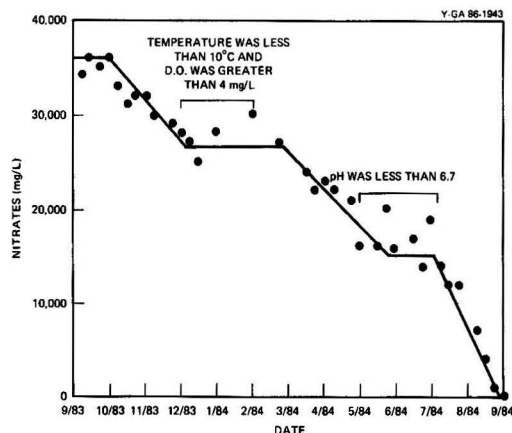


Figure 5. Nitrate concentration, northeast and southeast ponds.

from the southwest pond, and the procedures for introducing chemicals were the same as in the test run. The initial pH, however, was less than 2.0 and the initial nitrate concentration was over 40,000 mg/L, thus requiring larger quantities of chemicals for neutralization and bio-denitrification.

Calcium carbonate was added over a 5-day period and the pH was increased to 4.7. Large amounts of solids precipitated as a result of the pH increase. The pH was then raised to 9.0 with calcium hydroxide added through direct pneumatic feeding into the pond. After addition of less than 50% of the required amount of acetic acid, the pH dropped below 4.0. The pH was adjusted with calcium hydroxide, and the rest of the acetic acid was added intermittently in small amounts. After denitrification began, a gradual pH drop was noted, which was controlled through intermittent additions of hydroxide.

Denitrification began shortly after acetic acid addition and neutralization (Figure 4). Nitrate concentrations decreased to a 28,000 mg/L level and then stabilized. Concurrent with this, lower water temperatures were recorded as a result of the onset of winter. There were no denitrification during the winter months (November to February). When water temperatures increased above 10°C, microorganisms resumed their activity and the bio-denitrification reaction proceeded until May 1984. At that time, a drop in pH resulted in no further denitrification taking place until the pH was adjusted. Almost immediately after the pH adjustment, denitrification began and the remaining nitrates were destroyed within a 60-day time period.

NORTHEAST AND SOUTHEAST PONDS

In September 1983, piping and pumps were installed in the northeast and southeast ponds so that both ponds could be treated as one. Neutralization was completed using the same procedure as with the northwest pond. Results observed in these ponds were similar to those for the northwest pond (Figure 5). Similar pH and temperature effects were noted. Initial nitrate concentration of 36,000 mg/L was recorded, with a final reading in September 1984 of 10 mg/L.

SUMMARY AND CONCLUSIONS

Large amounts of nitrate wastes have been denitrified in open ponds at the Oak Ridge Y-12 Plant. The process consisted of neutralization followed by biodenitrification and bio-oxidation. Neutralization was accomplished mainly through the addition of calcium carbonate and cal-

cium hydroxide. Most dissolved metals in the waste were precipitated through neutralization. Biological denitrification was accomplished, after neutralization, through the addition of acetic acid as a carbon source at a 1.3 to 1 carbon to nitrogen weight ratio. After acclimation, denitrification proceeded until the remaining nitrate was less than 50 mg/L. *In situ* denitrification was accomplished with beginning nitrate concentration of over 40,000 mg/L. Following denitrification, bio-oxidation was utilized to decompose the remaining organic material in the water. Through this process, a substantial reduction in the remaining carbon was recorded, although refractory organics not amenable to aerobic microbial oxidation remained.

No difficulties were observed in denitrifying in the open air. Dissolved oxygen concentrations diminished rapidly and remained low during denitrification. The presence of some oxygen in the water was not inhibitory to the denitrification reaction. The system was very sensitive to drops in pH below 6.8 and calcium hydroxide additions were necessary to adjust the pH, which consistently tends to be lowered through the addition of acetic acid and the abundant generation of carbon dioxide. Biological activity was noted to stop during the winter months when the water temperature was 10°C or lower. Denitrification proceeded normally once the temperature of the waste increased above the stated limit.

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Control of Emissions From an Air Stripper Treating Contaminated Groundwater

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The performance and costs of two well water treatment systems are compared: an aqueous-phase granular-activated-carbon (GAC) system, and an air stripping system with emission control. Both systems were installed to remove volatile organic compounds (VOC's) from the Verona Well Field, which supplies potable water to Battle Creek, Michigan.

INTRODUCTION

Many communities throughout the United States and the rest of the world have discovered that their groundwater is contaminated with volatile organic compounds (VOCs). This contamination can result from activities such as:

- Intentional application to soil, as in the case of volatile pesticides such as EDB and DBCP
- Poor disposal practices
- Leaking underground storage tanks

Air stripping has become a common treatment technique for removing VOCs from contaminated water supplies; however, it frequently is pointed out that this technique only transfers the contaminants from the water into the air. In response to this criticism of air stripping, several states are regulating the emissions allowed from air strippers.

This paper presents one case history of an air stripper installed at the Verona Well Field site, a Superfund site in Michigan where air emission control was required. Costs of installing and operating the air stripping system with emissions control are compared with costs for a temporary aqueous-phase, granular-activated-carbon (GAC) treatment system used at the same site.

BACKGROUND

The Verona Well Field supplies potable water to most of the residents and industries of Battle Creek, Michigan. In routine testing in mid-1981, the well field was found to have detectable levels of VOCs.

Initially, the city was able to maintain a supply of uncontaminated water by shifting pumping to the north, away from the advancing contaminant plume. By February 1984, however, it was apparent that the city would not have enough uncontaminated water to meet the summer maximum-day demand.

REMEDIAL MEASURE

The U.S. Environmental Protection Agency (EPA), as part of the Superfund program, tasked CH2M HILL to

begin a fast-track feasibility study of alternatives for alleviating the expected shortage of uncontaminated water. The fast-track study recommended a remedial measure that consisted of two parts:

- Install three new water supply wells and 4,000 feet (1.25 km) of forced main to deliver 6 mgd (22.7 ML/day) of uncontaminated water to the existing city pump station.
- Pump 2,000 gpm (7.57 m³/min) of contaminated water from a series of five existing water supply wells, thus using those wells as blocking wells to form a hydraulic barrier against further spread of contaminants into the well field. An air stripping system was recommended as the cost-effective method of treating the water before discharge to the nearby Battle Creek River.

The project schedule called for installation of the air stripping system and the new water supply wells 4 months from start of design, in time to meet the expected peak water demand in August 1984. However, to prevent further spread of contaminants into the well field during the interim, the EPA ordered a separate and immediate action: begin operating the blocking wells before the air stripping system was in place. This action involved a temporary treatment system using aqueous-phase, granular-activated-carbon to treat the water for river discharge. The action was coordinated with design of the air stripping system to ease interfacing, once the air stripping system was completed.

When any new source of known or suspected carcinogens are involved, Michigan air quality regulations require that the best available control technology be applied to the air discharge. In this instance, vapor-phase activated carbon was determined to be the required control technology. Still, air stripping with emission control was determined in the feasibility study to be a more cost-effective treatment technique than was direct aqueous-phase adsorption.

This case history has provided an opportunity for a side-by-side comparison of aqueous-phase adsorption against air stripping with emission control. The main features and operating experiences for each system are described below, followed by a comparison of the costs incurred in installing and operating each system.

TABLE 1. AQUEOUS-PHASE GAC PROPERTIES

Carbon Source	Bituminous (reactivated)
Iodine Number	750 (minimum)
Bulk Density	30 lb/ft ³ (480 kg/m ³)
Particle Size	8 × 40 mesh
Ash	9 percent (maximum)

AQUEOUS PHASE GAC SYSTEM

System Description

Installation of the temporary aqueous-phase GAC, or carbon, system began on April 20, 1984. The project included constructing a pump station with wet well and dry well arrangement, connecting the appropriate municipal wells to the wet well, setting up the carbon adsorbers, connecting the new pumps to the adsorber inlets, and installing a gravity discharge line from the adsorbers to a nearby storm sewer that delivered the treated water to the Battle Creek River. The system was started up on manual operation on May 25; the level control system was completed on May 29. The carbon treatment system initially consisted of four adsorbers in parallel. Each adsorber was a standard 10-foot (3.05 meter) diameter vessel that contained 20,000 pounds (9,072 kg) of carbon. The carbon had the properties shown in Table 1. Shortly after startup, it became apparent that the wells were producing more flow than their rated capacity. Discussions with city operating personnel revealed that the actual combined capacity of the blocking wells was closer to 2,500 gpm (9.46 m³/min) than to the rated capacity of 2,000 gpm (7.57 m³/min). This resulted in rapid increases in pressure drop through the beds and required frequent back-washing. To accommodate the higher flow rate, a fifth adsorber was leased, and brought on line June 13, approximately 3 weeks after system startup.

GAC System Performance

The aqueous-phase carbon system was operated through September 20, 1984, nearly 17 weeks after the system was started up. The air stripping system was available before that time; however, the effluent from the aqueous-phase carbon system was still of suitable quality, and thus it was decided to operate that system until the aqueous-phase carbon was more fully utilized. The per-

TABLE 2. AQUEOUS-PHASE CARBON ADSORPTION CAPACITY

Compound	Avg. Influent Conc. (μg/L)	Mass Adsorbed (kg)	Adsorption Capacity (mg/gm)
1,2 Dichloroethylene	11	17.2	0.4
1,1 Dichloroethane	9.8	15.4	0.4
1,1,1 Trichloroethane	15	23.6	0.5
Trichloroethylene	2	3.1	>0.05*
Tetrachloroethylene	14	21.8	>0.5*
1,1 Dichloroethylene	1.4	2.2	>0.05*

* Contaminant had not yet broken through the carbon bed.

formance of the aqueous-phase carbon system is shown in Figure 1, which graphs influent and effluent concentrations of total VOCs over the period of operation. Influent concentrations averaged about 60 μg/L over the entire period. Influent concentration initially was significantly higher, but leveled off after about the sixth week at about 50 μg/L. The mixed effluent concentration increased steadily over the operation period until, at termination, total VOCs were at about 10 μg/L.

The five carbon adsorption vessels were designated as adsorbers A through E, with adsorber E being the adsorber delivered about 3 weeks after the original four. Four of the adsorbers exhibited very similar effluent quality. However, as shown in Figure 1, adsorber B produced substantially higher effluent concentrations than the other adsorbers did throughout the period of operation. The reason for this was not determined.

Table 2 shows the apparent adsorption capacity of the aqueous-phase carbon for each of the contaminants through the time when the run was terminated. Three of the contaminants (1,2 DCE, 1,1,1 TCA, and 1,1 DCA) had reached breakthrough. The effluent contained each of those constituents at concentrations approximately 30 percent of influent by the end of the period. The other three contaminants had not yet broken through, so capacities are reported as minimums; it is possible that actual capacities for those compounds would be substantially higher.

AIR STRIPPING SYSTEM

System Description

The air stripping system consisted of a countercurrent packed tower, an induced draft fan, an air heater, and two

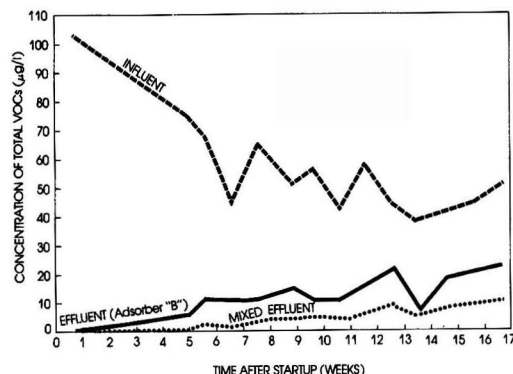


Figure 1. Influent and effluent concentrations of aqueous-phase adsorbers.

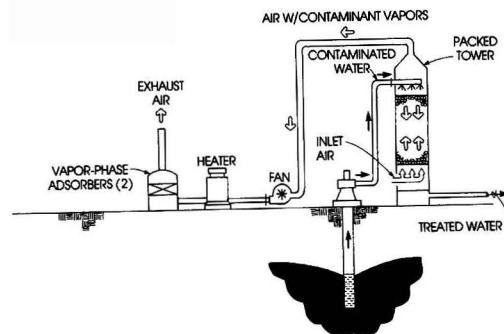


Figure 2. Packed tower with emission control.

TABLE 3. AIR STRIPPING SYSTEM DESIGN PARAMETERS

Packed Tower	Air Heater
Diameter: 10 ft (3.05 m)	Type: indirect fired
Overall height: 65 ft (19.8 m)	Fuel: natural gas
Packing type: 3.5-in. (8.9-cm) pall rings	Rated duty: 250,000 Btu/hr (73 kW)
Packing material: polypropylene	Vapor-Phase Adsorbers
Number of packed beds: 2	Diameter: 10 ft (3.05 m)
Height of each bed: 20 ft (6.1 m)	Number: 2
Water flow: 2,500 gpm (9.46 m ³ /m)	Bed depth: 4 ft (1.22 m)
Airflow: 5,000 scfm (141.5 m ³ /m)	Carbon: Calgon, type BPL, 4 × 6 mesh
Tower construction: FRP	
Fan	
Rated capacity: 5,500 acfm (155.6 am ³ /m) at 19-in. H ₂ O (48.2-cm H ₂ O)	
Power requirement: 20 hp (15 kW)	

vapor phase carbon adsorbers. Figure 2 is a schematic of the system showing the flow configuration of the major elements. Design parameters for the system are summarized in Table 3. The packed tower was considerably taller than would be used without the requirement for air emission control. Use of the tall tower with 40 feet (12.2 m) of packing allowed a low air flow rate to be used and thereby reduced the capital and operating costs of the emission control system. The air heater was included to reduce the relative humidity of the tower offgas by heating it from 50°F to 80°F. This was considered necessary to reduce the interference of water vapor with the adsorption capacity of the vapor phase carbon.

System Performance

The air stripping system was ready for operation on August 5, 1984, and was given a performance test that showed it would meet all design and permit requirements. As discussed previously, it was then shut down to allow further operation of the aqueous-phase carbon system until the carbon was more fully utilized. The stripping system was put into full-time operation on September 20, 1984. The system consistently removed contaminants from the groundwater to levels below conventional detection limits. Air emissions from the emission control system approached permit levels in a test taken on August 5, 1985, and the vapor phase carbon was subsequently replaced.

Carbon changing was accomplished using a vacuum system to remove the spent carbon from the adsorption vessels. Fresh virgin carbon was then dumped into the vessels, and the system restarted. Spent carbon was custom-reactivated and stored offsite for later delivery to the site. In this way, future carbon changes will require only the exchange of reactivated carbon for spent carbon. This procedure saves considerably on carbon cost and avoids the alternative of disposing of spent carbon as a solid hazardous waste. Influent concentrations to the system have remained fairly constant at about 40 µg/L since startup. Table 4 shows the concentrations of each of the constituents and the total VOCs reported from sampling and analysis.

The influent concentration data was used to calculate apparent adsorption capacities for each of the constituents on vapor phase carbon. Results of the adsorption capacity calculations are shown in Table 5. For those compounds that reached breakthrough, capacities were nearly ten times greater on vapor phase carbon than was

TABLE 4. AIR STRIPPING SYSTEM CONCENTRATIONS OF VOCs IN INFLUENT

Date	Elapsed Time (weeks)	Contaminant Concentration (µg/L)					
		1,1 DCA	1,1,1 TCA	1,2 DCE	TCE	PCE	Total
9/20/84	0	6.4	12.0	14.0	1.4	10.0	43.8
10/5/84	2.1	5.2	10.2	9.7	1.1	8.0	34.2
10/31/84	5.9	6.0	8.3	10.5	1.1	7.6	33.5
12/12/84	11.9	6.4	12.0	11.0	ND*	8.0	37.4
1/21/85	17.6	5.8	13.0	10.0	1.1	8.4	38.3
2/4/85	19.6	5.7	13.0	12.0	1.3	9.2	41.2
3/11/85	24.6	6.2	10.8	12.0	1.3	7.9	38.1
4/8/85	28.6	4.4	9.4	8.3	1.1	7.2	30.4
5/13/85	33.6	5.9	14.5	11.5	1.2	10.0	43.1
5/28/85	35.7	4.8	12.0	9.3	1.1	11.0	38.2
7/8/85	41.6	6.9	15.0	15.0	1.7	13.0	51.6
8/5/85	45.6	5.2	15.5	10.0	1.3	9.9	41.8
Average		5.7	12.1	11.1	1.1	9.2	39.3

* ND = no data.

TABLE 5. VAPOR PHASE CARBON ADSORPTION CAPACITY

Compound	Influent Concentration		Mass Adsorbed (kg)	Adsorption Capacity (mg/gm)
	Aqueous (µg/L)	Vapor (mg/m ³)		
1,2 Dichloroethylene	11	0.74	45.3	5
1,1 Dichloroethane	5.7	0.38	24.5	3
1,1,1 Trichloroethane	12	0.80	49.9	6
Trichloroethylene	1.1	0.07	4.5	>0.5*
Tetrachloroethylene	9.2	0.62	39.4	>0.5*

* Contaminant had not yet broken through the carbon bed.

observed on aqueous phase carbon. This suggests that the carbon replacement rate for the air stripping system would normally be about one-tenth that for the aqueous phase adsorption system.

COST COMPARISON

The cost of carbon replacement is certainly a major cost of treating contaminated water with both of the systems described above. However, several other significant costs must be compared before drawing a conclusion about the cost-effectiveness of the two systems. Actual installation and operating costs for the two systems are presented below, followed by a comparison of the two costs.

TABLE 6. AQUEOUS PHASE GAC SYSTEM MAJOR COST ITEMS

PUMP STATION COSTS	
Installed Cost	\$226,000
(includes equipment, materials, installation, and design)	
Pump Power Requirement	50 hp (37 kW)
ADSORBER COSTS	
Equipment Set-up and Testing	\$ 40,000
Activated Carbon	108,000
Spent Carbon Removal	12,000
Equipment Rental	50,000
Equipment Removal	15,000
Sampling and Analysis	17,000
Total Adsorber Costs	\$242,000

TABLE 7. AIR STRIPPING SYSTEM MAJOR COST ITEMS

PUMP STATION COSTS	
Installed Cost	\$226,000
(includes equipment, materials, installation, and design)	
Pump Power Requirement	50 hp (37 kW)
AIR STRIPPING SYSTEM COSTS	
Installed Cost	\$700,000
(Includes equipment, materials, installation, and design)	
Replacement Carbon (virgin)	32,000
Carbon Transportation and Replacement	3,000
Carbon Reactivation and Storage	14,000
Total Air Stripping System Costs	\$749,000
Fan Power Requirement	20 hp (15 kW)
Heater Natural Gas Requirement	250,000 Btu/hr (73 kW)

TABLE 8. COST COMPARISON—3-YEAR BASIS

Cost Item	Aqueous-Phase Carbon System	Air Stripping System
Initial Cost	\$ 374,000	\$ 926,000
Monthly Rental	360,000	0
Carbon Replacement		
5 changes at \$120,000	600,000	N/A
2 changes at \$17,000	N/A	34,000
Power cost @ 6¢/kWh	80,000	110,000
Natural gas cost	N/A	33,000
@ \$5/MM Btu (1.055 × 10 ⁶ ft)		
Total 3-Year Cost	\$1,414,000	\$1,103,000

Note: N/A = Not applicable

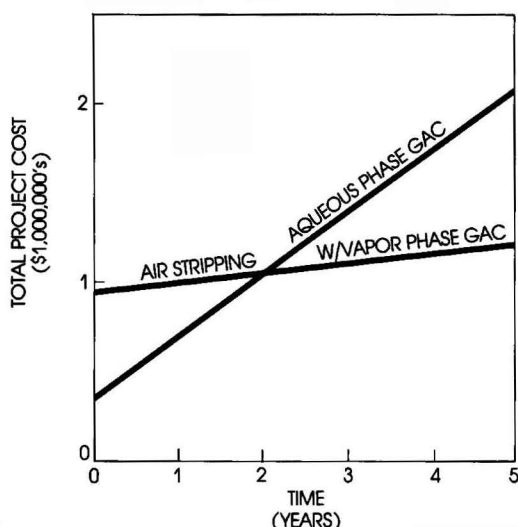


Figure 3. Cost comparison.

Aqueous Phase GAC System Costs

The aqueous phase carbon system consisted of two major components:

- The pumping station, including wet well, dry well, pumps, and associated piping and wiring
- The skid-mounted prepiped adsorption modules and associated pipe runs to the units

The major elements involved in installing and operating these two system components are presented separately in Table 6.

Air Stripping System Costs

Major cost items involved in installing and operating the air stripping system are shown in Table 7. Costs are shown for two system components, as explained below.

- The pump station costs are included in the costs of the air stripping system for purposes of comparing of the two systems.
- The air stripper and emission control system include packed tower, fan, air heater, adsorbers, and associated piping, ductwork, structural, electrical, and instrumentation.

Ideally, Table 7 would include a breakdown showing separate costs for the air stripper and the emission control system. However, the entire air stripping system was procured as a single equipment package and no breakdown of costs was obtained from the supplier. It is estimated that 50 to 60 percent of the cost was for the air stripper, and the balance of the cost was for the emission control system.

Comparison of Costs

The cost items presented in Tables 6 and 7 are not on a consistent basis that would allow direct comparison. The aqueous-phase carbon system was operated for 4 months and removed. The air stripping system was operated for nearly a year before the carbon was changed, and then was put back into operation. For purposes of comparison, Table 8 shows total costs that would be expected for each system if it were operated for 3 years. Because of the short time frame, the costs are totalled without discounting for

the effect of timing of expenditures. As the table shows, the aqueous-phase carbon system would be more expensive to operate for a 3-year period.

Figure 3 shows how the comparison between these systems would change, depending on the length of time the selected system were to operate. This analysis is presented without discounting for time effects. A discounted cash flow analysis would tend to favor the aqueous-phase carbon system because of its lower capital and higher annual costs, but the effect would be slight because of the short project life used in the analysis. As shown in Figure 3, at a project life of about 2 years, the costs of the two systems would be comparable. For shorter project life, the aqueous-phase carbon system would result in lower costs; longer project life would favor the air stripping system.

The comparison shown in Figure 3 is still not on a consistent basis, because the aqueous-phase carbon system was rented and the air stripping system was purchased. However, it is common in considering remedial responses of this nature to compare these two alternatives. Had the aqueous-phase carbon system been purchased instead of rented, the initial cost of the system would have been higher, but still less than that of the air stripping system. The annual cost of operating the aqueous-phase carbon system would have been less if it were purchased, but only by about 30 percent. The net result would have been a similar interaction in Figure 3, but at a slightly different point in time. It should be pointed out that both of these systems were installed under very severe time constraints. Had the system been installed under more comfortable delivery and construction schedules, it is likely that the costs of each system would have been reduced substantially.

CONCLUSIONS

The following conclusions can be drawn from this work: Both aqueous-phase carbon and air stripping with emission control are workable methods of removing volatile chlorinated hydrocarbons from water.

In this instance, if the treatment system were required to operate for longer than about 2 years, the air stripping system with emission control would result in the lower total project cost. For shorter operation periods, the aqueous-phase carbon system would be lower in cost.

The results are difficult to apply to VOC removal in general. For example, if the project involved less volatile constituents requiring a higher air flow rate, the cost of installing and operating the emission control system would increase dramatically. Such a situation would tend to favor the aqueous-phase carbon system.

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Municipal Solid Waste Composition and the Behavior of Metals in Incinerator Ashes

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Disposal of solid and hazardous wastes has become a concern in recent years. Incineration is a promising option for both, however, there are questions of public health effects and environmental acceptability of incinerator outputs. Ideally, operating conditions could be controlled to limit toxicity of residuals; to develop process models and feed-back algorithms requires knowledge of the causal relationships between input and output to quantify induced responses.

The composition of municipal solid wastes (MSW) from residential service areas was categorized and residuals from MSW incineration were examined for metal content and leachability. Sample size, sampling methodology, segregation by category and homogeneity of service area were determined to be dominant factors influencing the composition of MSW. There were notable differences in metal content of the fly and bottom ash residuals.

Lead and zinc were the dominant trace metals in both ash residuals. Concentrations of cadmium and lead leached from the flyash were found to exceed EP limits. Lead and cadmium of both bottom ash and flyash fail proposed TCLP extraction limits by even larger margins. Permanent elimination of high-temperature process ashes, classified as hazardous, must be demonstrated.

INTRODUCTION

Land disposal of municipal solid wastes (MSW) in landfills has been increasing in recent years. Current estimates indicate that 144 million tons per year (as generated, with moisture) of municipal wastes are disposed of in this fashion and it is predicted that approximately 197 million tons of municipal solid wastes will be generated in 1990 [1]. Under present solid waste management practices, wastes are primarily disposed of in approved sanitary landfills. In addition to overflow, there are the problems of leachate generation by the infiltration of rainwater and methane gas production due to decomposition. At present, federal, state and local governmental agencies are seeking alternative methods for the safe disposal of solid wastes.

Thermal destruction, i.e., incineration with or without energy or substance recovery, is a means of solid waste management of increasing importance. Incineration is also a preferred means for disposal of many industrial and hazardous wastes. This method of treatment destroys solid waste through oxidation, i.e., exposure of the solid material to high temperatures in the presence of air. The process results in the production of exhaust gases, solid residuals and contaminated quench and scrubbing waters. Ideally, the quality of these output streams should

be such that free discharge of the gases, straight-forward wastewater treatment and conventional landfilling of the solid residuals are possible.

Toxic organic species can escape quantitative destruction during thermal processing. Dangerous levels of PCBs have been detected in stack gases from rotary kiln incinerators. Other toxic organic species, specifically PCDDs and PCDFs, are believed to be formed during incineration and can appear in flyash and exhaust particulate matter. Inorganic species, including metals, metallic salts and oxides, SO_2 , NO , and HCl , pass through combustion or are formed and appear to various free and combined states in all residuals. Licensing and permitting procedures establish criteria for incinerator and resource recovery unit operations and allowable discharges. Periodic sampling, together with some continuous monitoring, are used to test system conformance. However, feedback for process management is poor for a few easily tracked species and non-existent for most.

The great and increasing masses of solid and hazardous wastes generated in the United States must be addressed. Thermal processes are clearly indicated, but lack definitive demonstration of environmental acceptability. Process control is based on operator experience at the interface between measured outputs and variable inputs. Only

the simplest "Black-box" feedback algorithms exist; however, these do not provide for differential response to measured outputs, rather they are designed for automatic or emergency shutdown. For thermal destruction to become universally acceptable, process models, feed-back control algorithms and efficient on-line computer control programs must be created. However, compositions and causal relationships must become available for incinerator feed operation and residues. This information is necessary to quantify responses to variations in mass flow and operating conditions.

Input compositions of solid wastes into an incinerator directly influence the composition of the solid and gaseous residuals. There is, however, limited literature available describing incinerator feed streams. MSW is one type of waste suited for incineration and, therefore, it is essential to categorize the composition and try to identify possible source influences and variations. In addition, it is also appropriate to analyze incinerator residuals from common, e.g., residential or commercial, sources to see if the resultant composition data is comparable. The focus of this study is metals in MSW from purely residential service areas and, for comparison, metals in solid residuals. In turn, it is necessary to report on similarities and trends in leachability data for metallic species to predict typical MSW ash behavior after disposal.

To simulate the mobility of inorganic constituents from wastes, the U.S. Environmental Protection Agency established a laboratory batch leaching test known as the Extraction Procedure (EP). The EP was promulgated under the authority of the Resources Conservation and Recovery Act of 1976 [2a]. This procedure employs the use of a dilute solution of acetic acid as the leaching medium. This volatile fatty acid is common in leachate from municipal waste, since it is a byproduct of the first stage of anaerobic degradation. However, there has been much recent criticism of the applicability of the EP. As a result of the criticisms, a new test was developed and proposed [2b]. The Toxicity Characteristic Leaching Procedure (TCLP) differs from the EP in that the extractant is either buffered acetic acid or dilute acetic acid depending on the initial pH of slurried solid. The extractant is introduced in one addition and the pH is no longer maintained externally. The extraction is run for 18 hours in a closed extraction vessel.

Both EP and TCLP methodologies have been used to evaluate incinerator ash behavior after landfilling. In summary, the control and effectiveness of thermal destruction is viewed from the prospective of metal content of municipal trash, incinerator ash metals and leaching potential under prescribed test conditions.

MUNICIPAL SOLID WASTE COMPOSITION

MSW composition varies as a function of socio-economic status, geographic location, season, collection patterns and recycling practices. The feed stream to an incinerator or resource recovery unit can be expected to vary widely during periods of operation as short as minutes. Eight references have been selected to illustrate this variability. Four studies were carried out for cities and counties of New Jersey [3, 4, 5, 6]. Three studies are cited because of special sampling, sorting or analytical data generated [7, 8, 9]. A recent reference is perhaps, the most complete; it includes data for nine political jurisdictions, nineteen overlapping constituent categories and a period of thirty-four years [10].

Categorical compositions of MSW are compared in Table 1. Sample size, sampling methodology, segregation by category and homogeneity of service area are dominant factors for composition determination.

Since combustible matter is the driving force for ther-

TABLE 1. CATEGORICAL MSW COMPOSITION (%)

Reference:	[3]	[4]	[9]	[6]	[10]
Newspaper	—	5.23	8.1	21.9	8.49
Paper	40.6	—	—	—	—
Corrugated	—	15.23	—	13.1	11.98
Mixed Paper	—	—	—	—	17.07
Paper Products	—	—	—	—	34.58
Other Paper	—	—	24.1	—	—
Diapers	—	—	1.1	—	—
Wood (lumber)	1.2	4.83	1.1	2.5	4.97
Plastic	8.6	5.65	—	7.8	6.24
Plastic, film	—	—	3.1	—	1.40
Plastic, rigid	—	—	2.2	—	—
Plastic, other	—	—	—	—	2.60
Yard Waste	—	—	39.7	19.7	19.02
Food Waste	—	—	3.1	—	8.52
Food & Yard Waste	11.7	—	—	—	—
Organics	—	37.19	—	0.6	—
Other Organics	—	—	—	—	19.79
Rags & Other	12.7	—	—	—	—
Sweepings	—	—	—	—	—
Textiles	—	—	4.0	—	3.39
Leather/Rubber	—	—	—	—	1.78
Miscellaneous	—	11.95	—	20.2	—
Total Combustible	74.8	80.1	86.5	85.8	—
Glass	15.8	7.33	3.4	6.7	6.95
Ferrous	6.3	6.53	3.1	2.7	4.92
Aluminum	2.0	1.17	0.3	3.4	1.20
Other Nonferrous	0.6	—	0.3	0.9	—
Other	0.4	4.78	6.4	0.4	—
Total	—	—	—	—	—
Noncombustible	25.1	19.8	13.5	14.1	—

mal processes, classification of this property of MSW is mandatory. Overall averages from studies at the Pennsauken (NJ) municipal landfill were chosen for citation, as follows [5]:

Combustibles	82.9%
Glass	10.7%
Ferrous Metals	4.7%
Nonferrous Metals	1.6%
Miscellaneous	0.1%

Proximate analyses have been reported for several geographic areas and MSW types [3, 4, 6, 10], with substantial cross-referencing among sources. Ash and moisture distribution in combustible constituents of MSW vary considerably [9]. Paper and Paper Products have a moisture content of 17-26% and dry ash residual of 1-5%; diapers are an exception in this category with in excess of 60% moisture. Typical values, with 95% confidence limits, were selected from a three county study carried out in anticipation of the 2500 ton/day Essex County (NJ) resource recovery plant [4]:

Total Moisture, %	24.7 +/- 2.6
Ash, %	23.6 +/- 2.2
Volatiles, %	44.9 +/- 2.8
Fixed Carbon, %	6.8 +/- 1.6
Heating Value, BTU/lb (moisture-free basis)	6500 +/- 250

Ultimate analyses have been equally broadly evaluated; distinctions between commercial and residential MSW are not as great for the six elements, reported as Ultimate analyses, as for Proximate analyses. Approximations for Ultimate analyses were taken from Essex, Hudson and Union Counties Study [4]. Selected values, with 95%

confidence levels, are as follows:

Carbon, %	42.8 +/- 2.5
Oxygen, %	21.1 +/- 0.4
Hydrogen, %	5.9 +/- 0.2
Nitrogen, %	0.8 +/- 0.1
Chlorine, %	0.5 +/- 0.15
Sulfur, %	0.2 +/- 0.05

Fractional composition is on a moisture-free basis.

Elemental distributions in MSW are highly variable. Waste source selection, sample preparation and constituent variations contribute to this problem. Elemental analyses obtained on samples from a municipal landfill (San Diego County, CA, 1981) have been selected [8]. Means and standard deviations for the residential MSW are, as follows:

Zinc, ppm	665 +/- 822
Lead, ppm	471 +/- 232
Molybdenum, ppm	28 +/- 8
Arsenic, ppm	11 +/- 4
Cadmium, ppm	11 +/- 17
Tin, ppm	6 +/- 10
Antimony, ppm	4 +/- 2
Selenium, ppm	0.6 +/- 0.2
Mercury, ppm	0.6 +/- 0.3

Although deviations are very high, this information serves as an indicator of probable incinerator feed stream characteristics.

ASH COMPOSITION

There are two types of solid residuals from incineration. Flyash is the gasborne particulate residue collected from incinerator flue gases using state-of-the-art air pollution control devices, e.g., venturi scrubbers and baghouses or electrostatic precipitators. Bottom ash is the heavier preliminary ash residual collected from the primary combustor, quench water and scrub water. Variations in metallic composition of these two types of ash are to be expected because of thermal history and metal chemistry.

It is clear from the table of elemental distributions in MSW that many of the metals classified as hazardous by EP Toxicity criteria are present in waste. Because of the

sorption characteristics of ash, and flyash in particular, as well as the volatilization/condensation properties of metals, the process of incineration tends to condense metal and metal oxides onto and within the ash particles.

Flyash can be recovered from incinerator flue gases as a powdery solid residue. Recovered ash consists largely of oxides or salts of silicon, aluminum, calcium, magnesium, iron and sodium. Compounds of titanium, barium, zinc, potassium, phosphorus and sulfur may be present in small amounts; trace quantities of organic compounds and many other elements can be present as well. Because of the presence of potentially soluble inorganic and organic species concentrated in and on the ash, flyash must be disposed of cautiously. To predict environmental impacts and to avoid leaching of contaminants into the environment, a complete understanding of the composition and chemical behavior of flyash is essential. Leaching of contaminants from landfilled ash is one of the pathways by which toxic substances can migrate to groundwater.

The concentrations of specific metals extracted from the ash provide information concerning matrix structure, which directly influences environmental contamination potential and feasibility of metal recovery. A variety of extraction solvents have been employed to probe the chemical behavior of incinerator flyash. The quantity and identity of metal present in the extraction solvent is dependent on the nature of the original waste, variations within the incineration process, the types and concentrations of solvents used and the mechanical methods of contact employed. These parameters are discussed in the selected references [11 through 21].

The composition and extractive behavior of flyash solids are dependent on the type and composition of waste incinerated. The incineration of municipal refuse will, of course, yield an ash different in structure and composition than would be obtained from sewage sludge. Less obvious, however, are the variations that exist within a waste type due to geographical factors, source characteristics, or chemical treatment prior to incineration.

One of the problems created by thermal waste disposal is the evolution of toxic organic substances in the effluent streams of an incinerator. Many studies have been done for quantification of the organic species which have been found to exist on flyash [20, 22, 23, 24]. These have been great concern over the discovery of some organochlo-

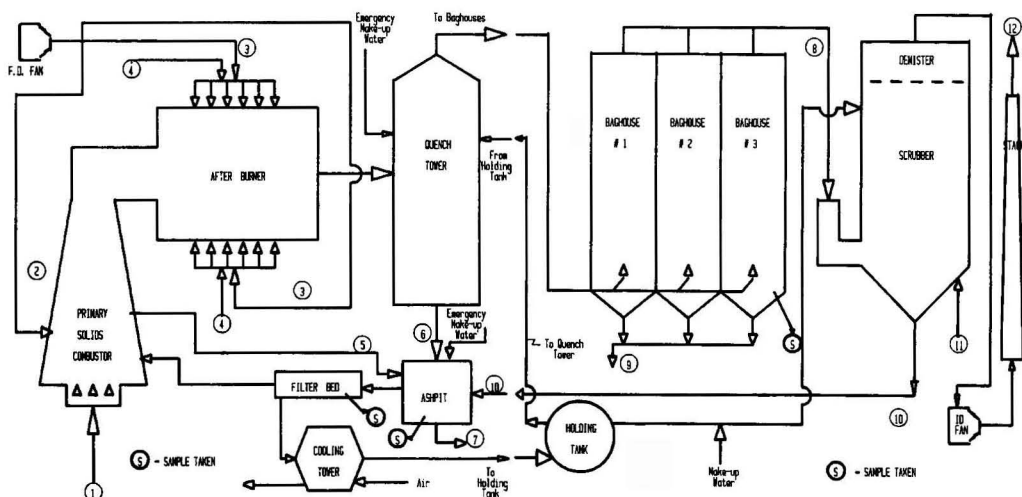


Figure 1. Graphic of the incinerator used to generate ash.

rides, especially polychlorinated dibenzo-p-dioxins (PCDDs), on flyash. Some PCDDs, notably 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD), have been found to be extremely toxic to animals in very small quantities [25].

It had been assumed that the high temperatures achieved in municipal incinerators (>800 C) would be effective in destroying any organic compounds in the refuse. As a matter of fact, this method has been used to dispose of organics such as PCB and PCDD [26, 27]. The mechanisms by which these species can escape destruction in a municipal incinerator have become of great concern. Knowing these mechanisms can be useful in designing a control scheme for a more environmentally safe incinerator.

A recent article by Taylor *et al.* reports the results of a series of samples of stack emissions from an incinerator. The system sampled is a steam boiler fueled solely by refuse [29]. Furnace temperature did not exceed 1350 F and, typically, the incinerator achieved 58% reduction in the weight of refuse received.

Three samples of stack emissions were taken by a Modified Method V train, in September 1981. A flyash sample was taken in parallel with the first stack sample. Total emissions were assayed and reported for four to six sample sub-types, i.e., front wash, back wash, trapped particles, etc. Assays were performed on isomer groups from Tetra- to Octa-CDD. Concentrations of CDDs, summed over all sample sub-types and tetra- to octa-substituted isomers, are referred to as Σ CDD. Tetra-CDD (TCDD) is believed to be the most toxic class of isomers. For comparison, data for the same classes of isomers on flyash *only* is found in the Arthur D. Little Inc. report to the ASME [24].

Based solely on flyash data, Σ CDD and TCDD vary over more than two orders-of-magnitude. This is certainly a reflection of waste composition and system operating conditions. Note, the energy recovery system observed by Taylor *et al.* is run at much lower temperatures than is an incineration system intended for maximum destruction and minimum solid residue recovery [29]. In 1985, an extensive study of PCDDs was completed in Canada and another was initiated by the ASME in Pittsfield, MA (USA).

In addition to the appearance of PCDDs in incinerator effluents, TCDD arises as a by-product and/or contaminant in the synthesis of solvents, e.g., chlorophenols, and herbicides. NIOSH recommends that TCDD be regarded as a potential occupational carcinogen [30. This statement is based on a number of carcinogenicity studies in rats and mice. The Centers of Environmental Health Sciences and Disease Control have adopted a similar position [28]. A dose of 0.0018 ng/kg, day may be tolerable.

APPROACH

A cooperating facility has been operating a 50 ton/day incinerator for several years. This system has over one hundred (100) measurement points. Measurements include temperature, absolute pressure, differential pressure and flow. Operating parameters are converted from analog to digital format and conditioned for storage and retrieval by on-site computer. Analog signals are integrated into an automatic shut-down procedure. If selected temperatures or pressures are exceeded, the system is shut-down without necessity of operator intervention.

The primary combustion chamber is followed by a secondary, after-burner. The after-burner temperature is adjusted with supplementary fuel; temperature and residence time are appropriate to four-to-six 9s destruction efficiencies for organic species in the waste feed stream. Combustion gases are quenched and scrubbed for tem-

TABLE 2. 1:1 HNO₃/HClO₄ DIGESTIONS: TOTAL METAL CONTENT

Municipality	Metal	Flyash (ppm)	Bottom Ash (ppm)
Pennsauken MSW 8/20/85-8/22/85	Cr	30	40
	Cd	490	100
	Pb	4990	6970
	Ag	<1	<1
	Ba	250	3255
	As	47	118
	Zn	4700	4400
Magnolia MSW 1/18/86-1/20/86	Cr	50	73
	Cd	130	5
	Pb	2838	650
	Ag	<1	<1
	Ba	218	5965
Somerset Co. MSW 2/12/86-2/15/86	As	80	71
	Cr	52	35
	Cd	227	8
	Pb	3993	852
	Ag	<1	<1
	Ba	1892	1906
	As	87	112

TABLE 3. EP TOXICANT EXTRACTION DATA

Municipality	Metal	Flyash (ppm)	Bottom Ash (ppm)	EP Toxicity Limits (ppm)
Pennsauken MSW 8/20/85-8/22/86	Cr	<1	<1	5.0
	Cd	15	<1	1.0
	Pb	27	3	5.0
	Ag	<1	<1	5.0
	Ba	<1	<1	100.0
	As	<1	<1	5.0
	Cr	<1	<1	5.0
Magnolia MSW 1/18/86-1/20/86	Cr	11	1	1.0
	Pb	28	3	5.0
	Ag	<1	<1	5.0
	Ba	1	2	100.0
	As	<1	<1	5.0
Somerset Co. MSW 2/12/86-2/15/86	Cr	2	<1	5.0
	Cd	11	<1	1.0
	Pb	5	1	5.0
	Ag	<1	<1	5.0
	Ba	<1	<1	100.0
	As	<1	<1	5.0

perature conditioning and sulfur dioxide (SO₂) removal. Cooled gases are passed through bag filters and discharged. It is possible to make continuous observations of stack gases for excess oxygen, carbon monoxide, carbon dioxide and residual hydrocarbons. Periodic samples of stack gas are taken for determination of particulate, SO₂, PCDD and PCDF concentrations.

Figure 1 is a graphic representation of the incinerator used to generate the ash assayed in this study. The MSW was collected from three different locals in New Jersey. Pennsauken and Magnolia are both townships where the waste is entirely of residential origin. The Somerset County waste is primarily residential but contains some commercial waste, also. The MSW is fed into a partially rotating primary combustor, followed by the secondary, fixed after-burner. Solid residuals from the primary solids combustor, quench tower and venturi scrubber all feed into an ashpit. Bottom ash is sampled from the ashpit and flyash is collected from three baghouses.

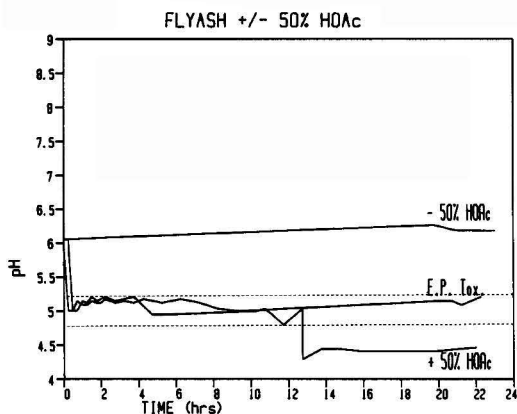


Figure 2. pH behavior during a twenty-four hour period.

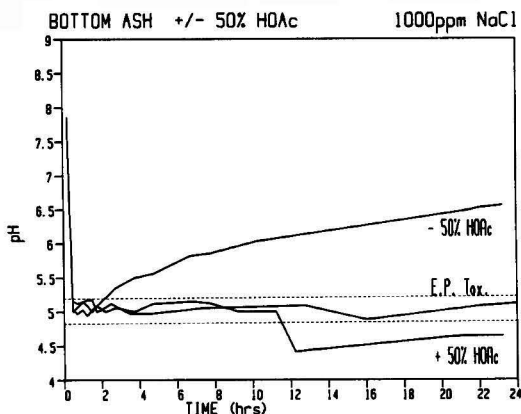


Figure 5. pH behavior during ionic strength variation experiments.

EXPERIMENTAL METHODS

Samples of ash were collected from demonstration burns of MSW generated from three separate communities in New Jersey. Samples of bottom ash and flyash were taken and assayed in parallel for direct comparison. For the first burn studied, the MSW was from Pennsauken, N.J., primarily a residential municipality. Beginning on August 20, 1985, grab samples of bottom ash were collected once every hour for thirty hours (the duration of the burn); two flyash grab samples were taken on August 22, 1985, at the conclusion of the burn. The samples were combined and mixed well to minimize the effect of heterogeneity of the bulk composite. On January 20, 1986, samples of fly and bottom ash were collected as composites, resulting from a three day burn of Magnolia, N.J. MSW. The hourly sampling and eventual mixing of the bottom ash was carried out by personnel employed by the incineration facility. On February 15, 1986, samples were again obtained as bulk composite, resulting from a burn of MSW from Somerset County, N.J.

Metal concentrations were determined by Atomic Absorption Spectroscopy (AAS). Dissolutions for total metal determinations were carried out in replicate using 1:1 nitric acid/perchloric acid sequential digestions. Two grams of ash were placed in the bottom of a 100 ml Kjeldahl flask. Twenty ml. of concentrated nitric acid were slowly added along with a few teflon boiling chips. The mixture was allowed to boil slowly for two hours. After cooling, 20 ml of 70 v/o perchloric acid were introduced and the mixture was reboiled for an additional two hours using a trap to catch any escaping perchloric acid fumes. The digested samples was filtered and diluted quantitatively to 100 ml. Elemental analysis was done with a Perkin Elmer 3030 Atomic Absorption Spectrophotometer (AA). All concentrations except that of arsenic were determined by flame AA analysis. Arsenic concentrations were obtained using flameless, Stabilized Temperature Platform Furnace (STPF) AA. Data for total metal concentrations for these ashes from the three burns of MSW are presented as Table 2.

Ten gram samples (in four replicates) of both the fly and bottom ashes were used in extraction experiments. Experiments were carried out with a methodology comparable to the Extraction Procedure Toxicity Characteristic [2a]. The solid material was weighed and placed in a beaker with deionized water, at a liquid-to-solid ratio of 16:1. An overhead stirrer equipped with a teflon stirring

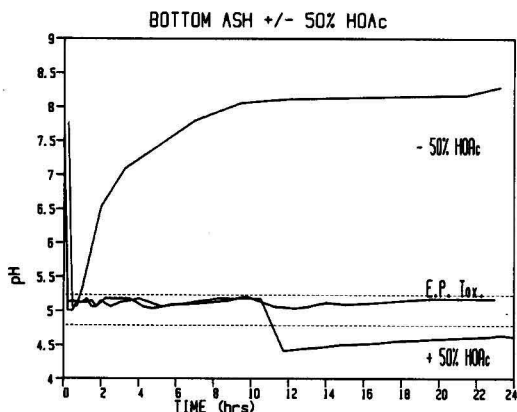


Figure 3. pH behavior during a twenty-four hour period.

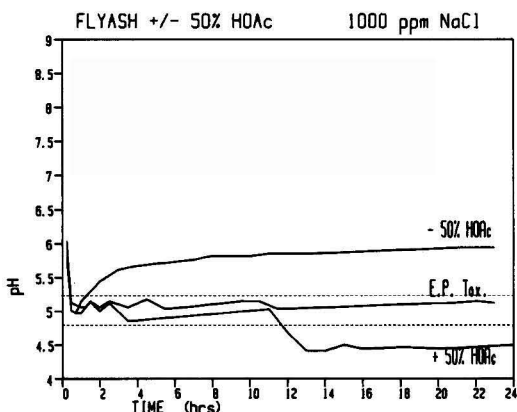


Figure 4. pH behavior during ionic strength variation experiments.

TABLE 4. SENSITIVITY OF EP EXTRACTION METHOD

Pennsauken Municipal Solid Waste 8/20/85

EP Toxicity Methodology: Addition of 0.5N Acetic Acid to stabilize pH at 5.0, not to exceed four times the sample weight; in 16 times the weight in water; with a quantitative addition of water to total a 20:1 extractant to solid ratio.

Variations: +/- 50% Acetic Acid addition in water

+/- 50% Acetic Acid addition in 1000 ppm NaCl.

Results;

	EP Tox. H ₂ O ppm		-50% HOAc H ₂ O ppm		+50% HOAc H ₂ O ppm		Ep Tox. NaCl ppm		-50% HOAc NaCl ppm		+50% HOAc NaCl ppm	
	FA	BA	FA	BA	FA	BA	FA	BA	FA	BA	FA	B
Cu	1	1	1	<1	3	2	2	3	1	1	—	—
Ni	1	<1	<1	<1	1	<1	1	<1	1	<1	—	—
Cr	<1	<1	<1	<1	1	<1	<1	<1	<1	<1	<1	<1
Cd	15	<1	14	<1	17	<1	15	<1	15	<1	<1	16
Pb	27	3	8	<1	35	5	32	4	12	<1	3	40
Ag	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ba	1	3	1	<1	1	<1	<1	<1	1	1	1	<1
As	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

* BA—Bottom Ash

* FA—Flyash

rod was used to provide sufficient agitation of the mixture. The pH of the solution was monitored during the course of the extraction; pH was maintained at 5.0 +/- 0.2 with 0.5N acetic acid addition, not exceeding 4 ml of acid per gram of ash. At the end of twenty-four hours, deionized water was added to bring the final mix to a 20:1 extractant-to-solid ratio. Experiments differed from EP in that ten gram composite samples were used, and the cadmium analysis was performed using flame atomic absorption spectroscopy rather than STPF, due to the high concentrations of cadmium present. Extractant metal concentration data is presented, in combination with EP toxicity test limits, in Table 3.

Ash residuals from the Pennsauken MSW burn were chosen to be the subject of EP Toxicant sensitivity studies. Experimental variations were introduced by doubling or halving the amount of 0.5N acetic acid used in the control experiment and subsequently letting the pH drift for the remainder of the 24 hour period. Figures 2 and 3 represent pH behavior. Repeats of these experiments were carried out with the addition of 1000 ppm NaCl to the extracting liquor. Figures 4 and 5 represent the pH behavior of these ionic strength variation experiments. Extraction variability data are presented as Table 4.

Experiments designed to simulate the TCLP [2b] were carried out on the same samples using ten grams of ash and 200 ml of extraction fluid. For the flyash, this solution (extraction fluid No. 2) was prepared by diluting 5.7 ml glacial HOAc with ASTM Type 2 water to a volume of one liter (pH 2.88 +/- 0.05). This extractant fluid was chosen, as opposed to a NaCl buffered solution, as specified by TCLP methodology. The pH of a solution of 5 grams of flyash in 96.5 ml of distilled deionized water exceeded 5.0. In turn, 3.5 ml of 1N HCl were added, the mixture slurried, covered with a watch glass, heated to 50°C and held for ten minutes. After cooling to room temperature, the pH was greater than 5.0, so extraction fluid No. 2 was chosen. The pH of a solution of 5 grams of bottom ash in 96.5 ml of distilled deionized water also exceeded 5.0, but after the 1N HCl addition, heating and cooling, the pH did not exceed 5.0. As a result, extraction fluid No. 1 was chosen. This solution was prepared by diluting 5.7 ml glacial HOAc to 500 ml with ASTM Type 2 water, adding 64.3 ml of 1.0N NaOH, and diluting to a volume of 1 liter. After eighteen hours of agitation (using the same apparatus as in EP methodology), samples were filtered and analyzed. Data is presented (in combination with both total metal concentrations and EP extractions, for comparison) as Table 5.

TABLE 5. TCLP EXTRACTIONS

Pennsauken MSW 8/20/85	HClO ₄ Digestions		EP Extractions		TCLP Extractions		EP (TCLP)	
	fly	bottom	fly	bottom	fly	bottom	limits	
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	
Cu	—	—	1	1	7	<1	—	—
Cr	30	40	<1	<1	1	<1	5.0	(5.0)
Ni	440	760	1	<1	<1	<1	—	—
Cd	490	100	15	<1	18	<1	1.0	(1.0)
Pb	4990	6790	27	3	44	<1	5.0	(0.2)
Ag	<1	<1	<1	<1	<1	<1	5.0	(5.0)
Ba	250	3225	1	3	2	2	100.0	(100.0)
As	47	118	<1	<1	1	1	5.0	(5.0)
Zn	4700	4400	—	—	—	—	—	—

RESULTS AND DISCUSSION

Samples size, sampling methodology, segregation by category and homogeneity of service area are dominant factors influencing composition determination of MSW. Combustible matter constitutes the majority of MSW and carbon is the major element present. Elemental distributions are highly variable.

The total metal content for fly and bottom ashes from the three municipalities are presented as Table 2. Differences in metal content of flyash and bottom ash are striking. Cadmium content was at least five times as great in the flyash as in the bottom ash. With the exception of the Pennsauken MSW, lead content was much greater in the flyash, also. Barium was much more prevalent in the bottom ash. Lead and zinc were the dominant trace metals in both ash residuals; however, since zinc is not classified as hazardous by EP Toxicity criteria, it was included only for comparative purposes in the data for total metal content of the Pennsauken ash. Barium concentration was second highest and cadmium was third in the flyash but second to last in the bottom ash. Arsenic and chromium were both proportionally consistent. Silver concentration was minimal in both residuals.

Incinerator temperature profiles representative of these burns, for both the solids combustor and the after-burner, are presented as Figures 6, 7, and 8. In general, incinerator temperatures remained above the desired minimums. Total metal content of the ash residuals were, for the most part, on the same order of magnitude for the three municipalities; this is reasonable considering that each of these wastes was primarily from domestic sources. There was some variation in the elemental data, however; specifically, the cadmium and lead content of the Pennsauken bottom ash and the barium content of the Somerset County flyash.

The concentrations of cadmium and lead leached from the flyash were found to exceed EP limits. The values obtained for bottom ash were acceptable with respect to cadmium, but marginal (in two of three instances) with respect to lead. It is also evident from the data that only a small fraction of the total metal content was extracted from the ash. An explanation for this type of behavior may be found by examining thermal metal chemistry. Cahill and Newland [11] group metallic species according to boiling point.

Elements with boiling points above typical combustion temperatures, (e.g. manganese, silicon and aluminum), are not likely to be volatilized in the combustion zone. Instead, during incineration, they form a uniform condensate that becomes the core of the ash matrix. By contrast, several trace metals, such as cadmium and lead, are largely volatilized at the high temperatures in the combustion zone and subsequently condense, at lower temperatures, onto the surface of this core matrix. Surface predominance is an important factor influencing the release of trace metals from ash. Elements deposited on surfaces (elements with low boiling points), typically exhibit higher extractability than core elements (elements with high boiling points). Compounds of the same element behave in a like manner [11]. Experimental data show that high concentrations of lead are found in the total metal extract solutions. The boiling points of $PbCl_2$, PbO and PbS are below $1550^{\circ}C$. This suggests that the lead extracted probably existed as one of these compounds; the remainder existing as lead metal. Following this reasoning, cadmium could be present as Cd , CdO or CdS .

Results of the variations in pH and ionic strength of EP methodology are presented as Table 4. Cadmium and lead were the most severely influenced of the metals. A higher pH lessened the percentage of extraction and con-

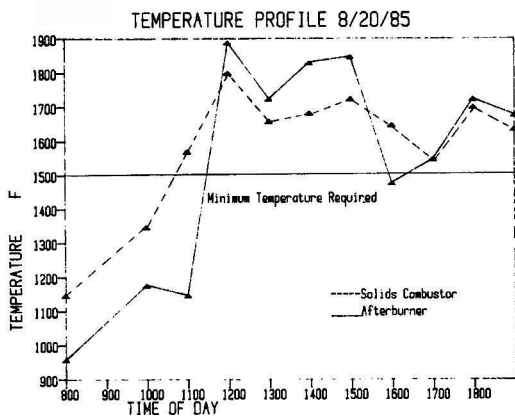


Figure 6. Incinerator temperature profile for both the solids combustor and the after-burner.

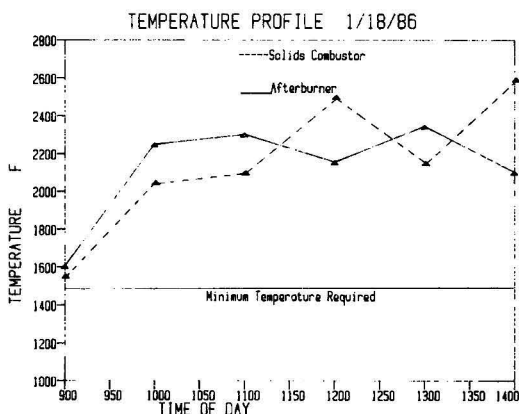


Figure 7. Incinerator temperature profile for both the solids combustor and the after-burner.

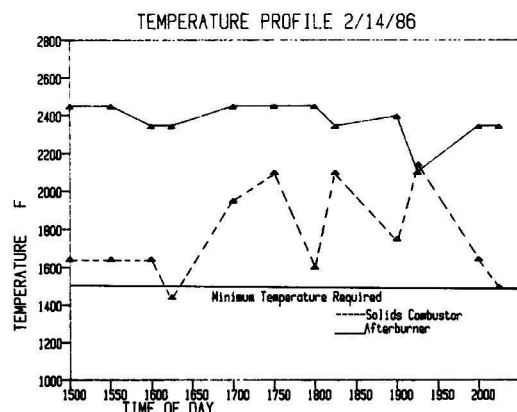


Figure 8. Incinerator temperature profile for both the solids combustor and the after-burner.

versely, a lower pH led to an increase. For cadmium, these influences were slight but, for lead, the influences were substantial. The decrease in acetic acid addition increased the extractant lead concentration to almost within EP toxicity limits for the flyash. For bottom ash, an increase in acetic acid addition increased the extractant lead concentration to the limit acceptability.

Because of partial factorial design and quadruplication of extraction experiments, a number of simple analyses of variance were possible. Variation in the quantity of acid used as a significant effect on lead leachability from flyash, at the 99% confidence level. This result is independent of experimental level of ionic strength. Acid addition has a significant effect on leachability of lead from bottom ash, also, but only with no salt added. With salt added, acid addition and lead leached from bottom ash are not correlated significantly. Responses of cadmium leached from flyash and bottom ash, to acid and/or salt additions, exhibit no statistical significance. In general, the results of applying EP methodology to incinerator ashes were not significantly influenced by the increase in ionic strength investigated.

The results of the TCLP extractions are presented as Table 5. These experiments can be considered an extension of the increase in acid quantity. The concentration of extraction fluid No. 2 of the TCLP is 0.1N. The final concentration of the increased acid extraction solution was approximately 0.02N. The results show the expected increase in the concentrations of cadmium and lead and, more important, an increase in chromium concentration.

CONCLUSIONS

Because of the complexity of residual ash matrices, the ability to predict surface deposition and subsequent extractive behavior of metals contained within the ash is essential. Metals known to be in high concentrations in influent MSW will not always be extractable from ash residuals. Conversely, low concentrations of some metals may be potentially hazardous. The high concentrations of cadmium and lead found in the flyash of MSW from primarily domestic sources poses a serious disposal problem. This problem is magnified when increases in acid concentration of the extractant liquor is examined.

Trends and similarities in the behavior of metals present in ash residuals exist. The challenge is to corroborate existing trends with alterable incinerator parameters to eliminate a problem of ash disposal.

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Recovery of Volatile Organics From Small Industrial Sources

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The recovery of volatile organic compounds (VOCs) from contaminated air generated by small industrial operations such as coating operations and spray painting is an important alternative to other air cleaning techniques such as thermal or catalytic incineration. Three technologies—adsorption, absorption, and condensation—are discussed herein. The focus of this article, and by far the most widely applied technique, is activated carbon adsorption. Commercial systems are generally designed for gas streams containing roughly 300 to 5,000 ppm VOC at flow rates from 200 to 100,000 ft³ (STP)/min (5.7 to 2,830 m³ (STP)/min).

General design parameters and costs, along with their application to example cases, are given for VOC recovery by activated carbon adsorption and condensation. No commercial systems specifically for VOC recovery by absorption have yet been reported, though this technology is extremely important for other air pollution control needs.

INTRODUCTION

The recovery of volatile organic compounds (VOCs) has become a concern in many industrial processes such as coating, printing, spray painting, textile finishing, and polymer processing for both economic and environmental reasons. These compounds are also found in some hazardous waste streams and are of concern since some treatment processes result in their release to the atmosphere. Usually, these compounds are present in dilute concentrations in air. These air streams can be treated either by thermal destruction methods or the VOC can be recovered. In many cases, though not all, recovery is less expensive.

This article describes the three generic technologies; adsorption, absorption, and condensation for the recovery of volatile organic compounds from gas streams generated by small industrial sources. Because it is the most economical way to recover VOCs from a wide range of gas streams encountered in the field, adsorption is by far the most widespread technology for VOC recovery and is the focus of this article. By choosing an appropriate sorbent and process configuration, many chemical types of VOCs can be recovered. Absorption can be used when the VOC concentration is relatively high and when an appropriate inexpensive absorbent liquid is available. Condensation can be energy intensive and is generally used for gas streams with high VOC content.

Treating a VOC-containing gas stream to recover the VOC(s) is only one of several broad alternatives to consider. Other alternatives that may be more economical include process modifications to reduce or eliminate the VOC content of the gas stream and using an ultimate destruction technique. A technical and economic evaluation

of available alternatives (recovery, process modification, or ultimate destruction) is a prerequisite to making the right choice for VOC control. It is the purpose of this article to discuss only recovery and to provide general guidelines for evaluation of the available recovery techniques for specific cases. VOC control techniques that are primarily means of ultimate destruction of the VOC, e.g., incineration or catalytic oxidation, are not considered.

PROCESS DESCRIPTION

Adsorption

Adsorption processes are extremely flexible for VOC recovery. By choosing an appropriate adsorbent and processing conditions, a wide range of VOCs can be recovered cost-effectively. For this reason, numerous commercially available processes have been developed for this purpose. For relatively small industrial VOC sources, systems are available that require a minimum of maintenance and operator attention. These systems are usually practical for small flow rates of VOC-containing gas (from several hundred to tens of thousands of ft³/min) and low VOC concentrations (usually several hundred up to several thousand ppm).

Figure 1 is a general schematic diagram of how adsorption is used for VOC recovery. Although the specific details of contacting between the gas stream and the adsorbent may differ among various systems, in principle all cyclic adsorption systems for VOC recovery can be represented by the process shown.* The VOC-containing gas stream is first conditioned by a particulate filter and perhaps a cooler/dehumidifier. It is then contacted with a bed of the sorbent material, usually a fixed bed of granu-

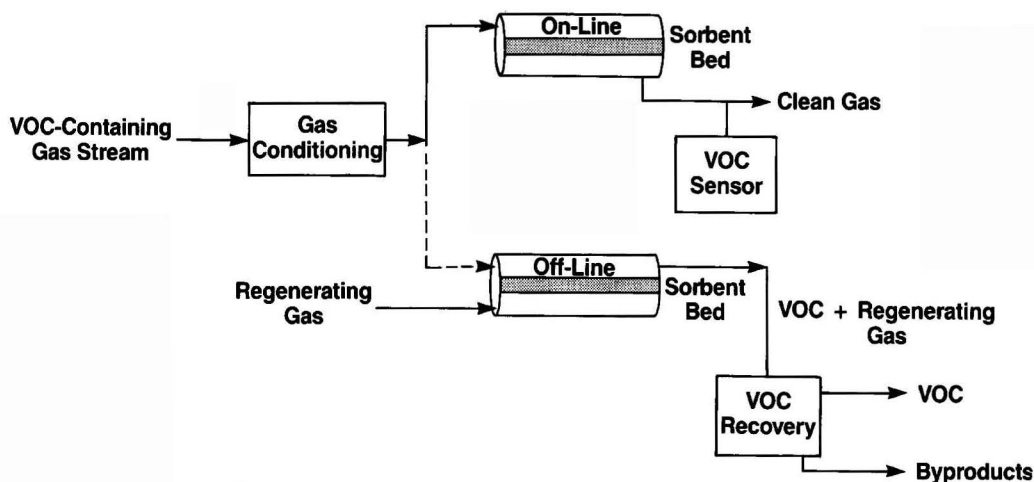


Figure 1. General process flow diagram of an adsorption process for VOC recovery.

lar activated carbon. The VOC is preferentially adsorbed from the gas stream and the clean gas leaves the sorbent bed. When the bed is exhausted, i.e., when the VOC concentration in the outlet gas stream exceeds a maximum acceptable level (this is called "breakthrough"), the bed is taken off-line for regeneration and the VOC-containing gas stream is diverted to a fresh (regenerated) sorbent bed. For continuous VOC removal, this implies the need for at least two, and perhaps more, sorbent beds operating in parallel. Regeneration of the spent sorbent can be done on-site (as shown), off-site by the sorbent vendor, or by a for-fee regeneration service. The most common method of regeneration is by low-pressure (~15 psig) steam. Other regenerating gases are sometimes used in special cases, for example if the adsorbate reacts with steam. If steam is used, heat released by condensation of the steam causes the VOC to desorb from the sorbent and the resulting vapor mixture is condensed downstream of the sorbent bed. The condensed liquid is allowed to separate into two phases. (In this case, the block in Figure 1 labeled "VOC recovery" would consist of a condenser and decanter.) The recovered VOC is then decanted and is available for reuse or sale. The aqueous phase can then be sent directly to wastewater treatment, subject to restrictions discussed below.

Absorption

Absorption is the transfer of one component of a gas mixture to a liquid due to preferential solubility of the gas in the liquid.** For VOC recovery, this process involves the transfer of the VOC from a gas stream to a suitable liquid in which the VOC is soluble.

In principle, almost all VOCs can be recovered from a

contaminated air stream by selection of an appropriate liquid absorbent and operating conditions. Although absorption is probably the most important gas-phase pollution control operation [7] (for removal of acid stack gases, for example), its use for VOC recovery from small industrial sources is not widely practiced [8]. Its relatively complex operation and the consequent cost account for its limited use.

Condensation

Condensation is the process of cooling a gas to a liquid form by transfer of heat. For the recovery of VOCs by condensation, this process involves cooling the VOC-containing gas stream to a temperature below the dewpoint of the VOC and collecting the condensed VOC directly as a liquid.

Condensation has been used for VOC recovery by small industrial users because of its simple operation, usually for low gas flow rates. The only equipment generally involved is a heat exchanger, which can be placed directly at the point of discharge and requires little, if any, operator attention. Since cooling water is often the most readily available coolant for condensation, and since its inlet temperature is normally at or above ambient temperature, VOC recovery by condensation using cooling water is limited to high VOC concentrations and higher-boiling VOCs. To recover low-boiling, low-molecular-weight VOCs requires refrigerated cooling, which can be expensive.

Figure 2 is a general process flow diagram of VOC recovery by condensation. The VOC-containing gas is first filtered to remove any particulates that could foul the heat exchanger surface over time. Heat is removed from the gas by indirect contact with the cooled surface of the condenser, and the VOC is recovered directly, either by simply collecting drops as they are formed, or by conventional demisters or cyclones which help coalesce the VOC droplets as they are formed.

* While all subsequent discussion of VOC recovery by adsorption is based on the type of system shown in Figure 1, two other types of adsorption VOC recovery systems are available. One involves adsorption under pressure with regeneration accomplished by pressure reduction. Such "pressure swing" systems are not generally used for VOC recovery, but in principle could be [1]. The second involves continuous contact of the gas and sorbent stream in a fluidized bed configuration. Such systems are not practical for the relatively low flow rates considered herein, but should be evaluated for larger flows (see reference 4, p. 701).

** Absorption is sometimes accompanied by chemical reaction or complexation of the absorbate (the soluble gas in this definition) with, or in, the absorbent. These processes are not generally applicable to VOC recovery, however.

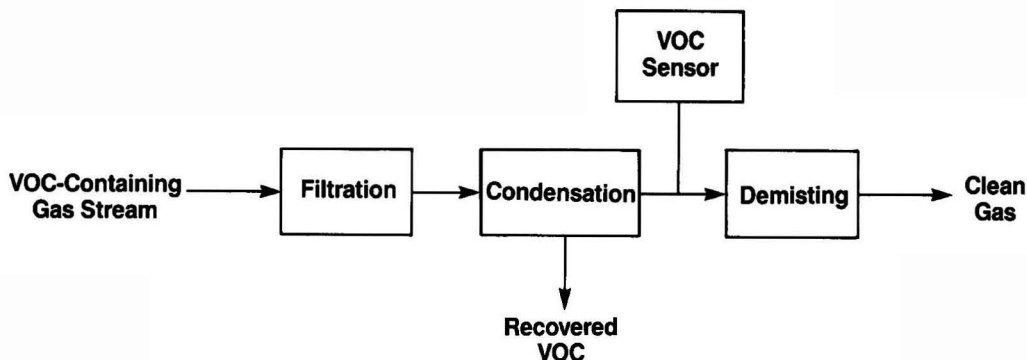


Figure 2. General process flow diagram of a condensation process for VOC recovery.

TECHNICAL CONSIDERATIONS

Figure 3 shows approximate ranges of VOC concentrations and flow rates to which the three technologies considered herein can be practically applied. Limits of application of these technologies are both technical and economic, and are discussed later.

Adsorption

To evaluate specific adsorption processes for a given VOC recovery need, the sorbent itself and the overall process design parameters must be considered.

Sorbents: In principle, many sorbents could be used for VOC recovery. These include activated carbon, molecular sieves, activated alumina, and activated silica. The only sorbent used in commercial VOC recovery systems is activated carbon. The preference for activated carbon is due to its relative insensitivity to water vapor, high surface area, high sorptive capacity for a wide range of VOCs, and low cost. Although other sorbents with suitable chemical and physical properties may exist, they have not yet been used in commercially available systems for VOC recovery.

The equilibrium between a VOC and a sorbent such as activated carbon can be adequately represented by an equation that expresses the weight of an adsorbate (i.e., a VOC) that can be adsorbed per unit mass of sorbent at equilibrium (W_i , in units of lb of adsorbate/lb of sorbent) as a function of the partial pressure of the VOC in the gas stream (P_i , in units of mm Hg) in a form known as the Freundlich isotherm:

$$W_i = \alpha P_i^{1/n} \quad (1)$$

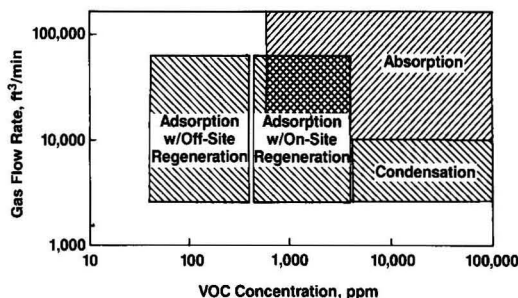
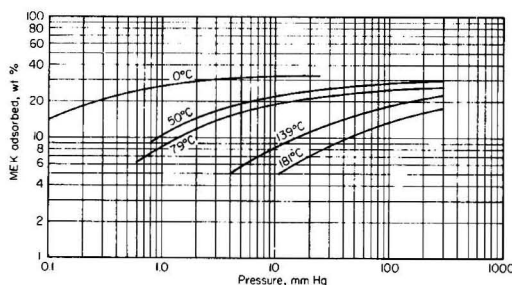
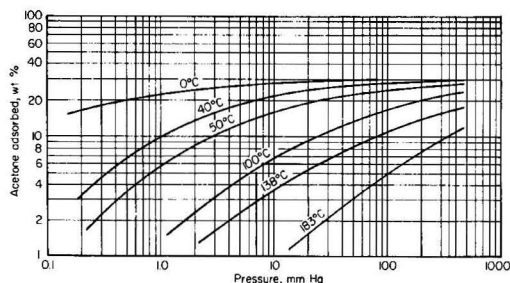


Figure 3. General ranges of VOC concentration and gas flow rate for selected recovery techniques.

where n is greater than 1. Both n and α are empirically determined constants, both of which generally decrease with increasing temperature. This suggests that a given sorbent will adsorb less of a given adsorbate (at equilibrium) at a higher temperature. This principle is used to regenerate a spent sorbent by heating it, with steam for example. The values of n and α are also unique to a given sorbent-adsorbate system. Because a unique relationship exists between a given adsorbate (e.g., a VOC) and a sorbent (e.g., activated carbon) at a given temperature, equation (1) is called an isotherm. Often, vendors will perform the necessary tests on a given VOC gas stream to determine the general shape of the isotherm if they do not already have experience with the particular gas composition. Kovach [5] gives a procedure for calculating the isotherm at any temperature knowing its shape at one temperature.



(a) Methyl ethyl ketone adsorption isotherms on Union Carbide 45 carbon.



(b) Acetone adsorption isotherms on Union Carbide 45 carbon.

Figure 4. Adsorption isotherms for two VOCs (from reference [5], p. 3-14).

Equation (1) is useful for any sorbent-adsorbate system and has found widespread use in practice. Figure 4 shows isotherms for two different VOCs on a commercial activated carbon sorbent. Note that equation (1) suggests that these log-log isotherms should be linear over all VOC partial pressures. Although the actual isotherms are not truly linear, equation (1) is an adequate approximation, especially since VOC recovery systems would normally be designed for a fairly narrow range of VOC partial pressures, usually about 0.23 to 3.8 mm Hg at 1 atm total pressure (300 to 5,000 ppmv).

Equation (1) and Figure 4 represent the quantity of VOC that can be adsorbed at equilibrium. This quantity is often called the "saturation capacity" by system vendors and is a function of temperature, the chemical and physical nature of the VOC of interest, and the VOC concentration of the gas in contact with a given carbon. This value for most activated carbons and VOC adsorbates is about 20-40% which means that the carbon can adsorb about 20-40% of its own weight at equilibrium (at a VOC concentration of 300 to 5,000 ppmv and a typical working temperature of 70 to 90°F). In practice, the carbon is designed to adsorb only about 25 to 50% of the "saturation capacity", or roughly 8 to 15% of its own weight, because not all the VOC is easily desorbed at practical operating conditions. This 8-15% adsorbate loading is called the "working capacity" and is the basis for all real system design.

The user should also be aware that because activated carbons are made from a wide variety of carbonaceous materials, including coal, coconut shells, wood, peat, and petroleum coke, physical and chemical properties can vary substantially from vendor to vendor as well as from batch to batch even from the same vendor. This variation does not reflect improper processing by the manufacturer but is inherent in the precursor materials.

In practice, it has been shown that in spite of the wide variety of activated carbons available and the wide range of VOCs to which this sorbent has been applied, there are limits to the types of VOCs that can be recovered. A review of technical and vendor information has shown that activated carbons are suitable for the following range of VOCs:

- (1) Those with molecular weights between roughly 50 and 200, corresponding to boiling points between about 68°F and 350°F
- (2) All aliphatic and aromatic hydrocarbons, subject to (1) above, i.e., carbon number between roughly C_4 and C_{14}
- (3) Most common halogenated solvents (subject to (1) above) including CCl_4 , ethylene dichloride, methylene chloride, perchlorethylene, and trichloroethylene
- (4) Most common ketones (acetone, methyl ethyl ketone) and some esters (butyl and ethyl acetate)
- (5) Common alcohols (ethanol, propanol, butanol).

However, several types of compounds are not suitable to activated carbon adsorption. These include compounds that react with the carbon itself or with the steam normally used for regeneration, those that polymerize on the carbon, or those that are difficult to remove in any practical regeneration step (e.g., high-molecular-weight compounds). Examples include:

Reactive compounds

- Organic acids (e.g., acetic acid)
- Aldehydes (e.g., formaldehyde)
- Some ketones (e.g., cyclohexanone)
- Some easily hydrolyzed esters (which react with steam, e.g., methyl acetate)
- Some halogenated hydrocarbons (if they hydrolyze easily e.g., ethyl chloride)

High-molecular-weight compounds

- Plasticizers
- Resins
- Hydrocarbons $>C_{14}$
- Phenols, glycols
- Amines.

Caution should be taken before ruling out carbon adsorption even for the above compounds, however. Process modifications can be made to permit economical recovery of these VOCs by carbon adsorption. As an example, the carbon can be regenerated with a hot inert gas such as nitrogen (instead of steam) to eliminate the hydrolysis reaction of some esters and halogens with steam. Vendors should be consulted for guidance on individual problems.

Typical System Design and Performance Parameters

Years of practice in the use of activated carbon adsorption for VOC recovery have led to general guidelines for system design and performance. The purpose of this section is to summarize these guidelines, first in terms of overall performance and second in terms of each major process step shown in Figure 1.

Overall Performance: Table 1 summarizes the major characteristics of a VOC-containing gas stream to which activated carbon adsorption can be practically applied.

As a rule, a well-designed carbon adsorption system for VOC recovery is suitable for handling gases with VOC concentrations of several hundred to about 5,000 ppm. The upper limit on VOC content is due to heat transfer limits and safety. Because adsorption is always an exothermic process (with a heat of adsorption roughly equal to the heat of condensation, Btu/lb VOC), the higher the VOC content of the inlet gas stream (e.g., lb VOC/lb incoming gas), the higher the total heat evolved when the VOC is adsorbed (Btu/lb incoming gas). As the VOC content of the gas increases, heat is evolved faster than it can be removed in a fixed-sorbent bed and the bed temperatures may rise to unsafe levels. The upper VOC concentration can also be limited by the explosive limits of the gas (usually air)/VOC mixture. One EPA report states that insurance companies limit inlet gas concentration to <25% of the lower explosive limit (LEL), unless special controls are added (in which case up to 40-50% of the LEL can be tolerated) [2]. The lower limit on VOC content is usually economic. At low VOC levels, it is not cost-effective to pay for the VOC recovery equipment because the bed will generally not become exhausted for quite

TABLE 1. PRACTICAL GUIDELINES FOR THE USE OF ACTIVATED CARBON FOR VOC RECOVERY

Item	Practical Limit(s)	Comments	Reference
VOC concentration	300-5,000 ppm	Limited by heat of adsorption (upper limit) and economics (lower limit)	2,4
Inlet gas temperature to sorbent bed	<100-120°F	Inlet temperature can be lowered before the sorbent bed, if necessary	2
Flow rate	200-100,000 ft ³ (STP)/min	May be higher in special cases	2
Relative humidity	<50% RH	If higher, a condenser can be used in the "gas conditioning" process	2

some time, in which case off-site regeneration of the sorbent is more economical. Activated carbon adsorption will still remove the VOCs even at inlet levels of several ppm; cost alone determines whether VOC recovery at these levels is reasonable. A level of several hundred ppm has been reported to be a practical economic limit [3, 4].

Temperatures at the inlet to the adsorption bed itself also have practical limits. Practice has shown that at temperatures above about 100 to 120°F, the heat of adsorption in the bed may result in insufficient removal of the VOC (this higher temperature corresponds to an isotherm at which the partial pressure of the VOC in the gas above the carbon is higher, as shown in Figure 4 for two VOCs). A quite wide range of flow rates is available in commercial systems [2] from several hundred to about 100,000 ft³ (STP)/min. The upper limit is one of practical size for a single given system, but there is no reason that multiple systems could not be used to handle any conceivably larger flow rate. The lower limit is again economic because on-site VOC recovery would be impractically expensive for very low flow rates, although in principle such a system would work.

The relative humidity of the inlet stream to the sorbent bed itself (downstream of any gas-conditioning process) must generally be less than 50%. Higher humidities may result in blockage of the small internal pores of the carbon particles and greatly reduce the carbon's working capacity.

Several factors can complicate the design of a carbon absorption system [3]. These factors, their effects, and possible solutions are shown in Table 2.

The major process components shown in Figure 1 are discussed briefly below along with practical design and performance parameters.

Gas Conditioning: Most commercial VOC recovery systems make provisions for gas conditioning to protect the sorbent bed. Depending on the composition of the raw inlet gas stream, the gas-conditioning process may consist of any or all of the following (these processes would logically be carried out in the order shown below):

- **Filtration**—The removal of particles down to 3 to 5 μ m is fairly straightforward. Finer particles may require special filters.
- **Dehumidification**—This is done to reduce the relative humidity to <50% and can be done with desiccants such as alumina or silica gel.
- **Cooling**—This may be done by refrigerated coil heat exchangers (which can also accomplish some measure of dehumidification) to reduce the temperature of the gas to 70 to 90°F.
- **Demisting**—This is the removal of aerosols (fine liquid droplets) and is accomplished with conventional demisters.

Sorbent Bed: The sorbent bed itself is generally capable of accomplishing an overall VOC removal of at least 95% and usually 99% or better [2, 3, 4]. Outlet VOC concentrations of 50 to 100 ppm can be achieved routinely and 10 to 20-ppm levels can be reached for many compounds. The working capacity of the bed, being a direct function of the equilibrium capacity as shown in Figure 4, is greater at lower temperatures. Thus, the lower the temperature of the inlet gas, the higher the working capacity of the bed. Also, as a general rule, unsaturated compounds (alkenes, alkynes, aromatics) are more strongly adsorbed than saturated compounds of similar carbon number. Thus, higher removal efficiencies will be obtained for these unsaturated compounds at given conditions.

The VOC concentration in the outlet stream will gradually increase with time after an initial break-in period of several days. Maintaining adequate removal efficiency requires periodic replacement of at least a portion of the

carbon bed. Proper system design should result in a carbon bed life of up to 5 years. This is accounted for explicitly below in the discussion of the economics of the carbon adsorption VOC recovery.

The carbon bed depth is usually between 1 and 3 feet [4] with 18 inches being typical. It is fixed by the need to achieve adequate mass transfer of the VOC to the pores of the individual carbon particles at typical linear gas velocities through the bed of 30 to 100 ft/min (with 50 ft/min being a good average value [3, 4]). This flow rate results in a pressure drop through the bed, for a normal granular activated carbon, of about 0.5 inch H₂O per inch of bed depth.

Beds are usually sized for an on-line "cycle" time of several hours. This is based on the time needed to desorb the VOC and dry the sorbent bed (if steam is used) in a two-bed system.

Steam usage (at 15 psig) for regeneration of most carbon/VOC combinations varies between 0.25 and 0.35 lb steam/lb carbon.

TABLE 2. COMPLICATING FACTORS IN CARBON ABSORPTION DESIGN

Factors		Effects	Possible Solutions
Presence of more than one VOC in the inlet gas stream	(1)	High-molecular-weight components displace lower molecular weight components, possibly reducing adsorption of these lighter VOCs	Increase sorbent bed size
	(2)	Recovered VOCs will be pure components if steam is used for regeneration. Decanting may be difficult if one VOC is heavier than water and one is lighter	Use distillation or some other fractionation process to purify recovered VOCs; use regenerating gas other than steam
Presence of water-soluble organics		VOC will not separate by simple decanting if steam is used.	Use distillation or some other fractionation process to purify recovered VOCs; use regenerating gas other than steam
Presence of reactive gases in the inlet gas stream		Carbon working capacity will degenerate irreversibly and sometimes rapidly	Remove the reactive gases in the gas conditioning process
Presence of corrosive gases in the inlet gas stream	(1)	Carbon working capacity will degenerate sometimes rapidly and irreversibly	Remove the reactive gases in the gas conditioning
	(2)	Sorbent vessel and piping may corrode	Use lined sorbent vessels or corrosion-resistant alloys
Presence of particulates or aerosols in the inlet gas stream		Carbon particles may become coated with small particles, irreversibly destroying their adsorptive properties	Filter the incoming stream

VOC Recovery: After the VOC has been adsorbed by carbon, it must be desorbed by a regenerating gas. The most widely used regenerating gas is steam, though off-the-shelf systems using hot air, nitrogen, or other gases are available for special cases.

If steam is used, the VOC recovery process of Figure 1 consists of a condenser and a decanter for gravity separation of the VOC and water. If the VOC is water-insoluble, this separation is simple and the VOC is recovered for reuse while the water is simply discharged without further treatment or is reused for boiler makeup. If the VOC is water-soluble and steam is used as the regenerant gas, then the VOC must be separated from the water, usually by distillation or extraction. Commercial systems are available to do this. Care must be taken to allow for removal of organics in the water to acceptable levels for discharge. Note that there are strict limits to the organic content of water acceptable to many municipal sewage treatment systems; usually, "percent" levels of organics are unacceptable. Very low levels must be achieved if the organic is toxic. One vendor has stated that the presence of water-soluble VOCs in the gas stream is probably the single biggest disadvantage to the use of carbon adsorption for VOC recovery [3].

If an inert gas is used to regenerate the bed, then the VOC may be recovered by condensation of the VOC from the presumably concentrated regenerating gas stream, or may be incinerated to recover its fuel value (this is not cost effective for halogenated solvents because they have low heating value, are corrosive to incinerator internals, and probably require costly flue gas treatment). Both types of systems are commercially available.

Absorption

While absorption is not used for VOC recovery from small industrial sources (EPA reports "... no known systems offered by equipment manufacturers" for at least some solvents [8], gas absorption is an extremely useful and widespread unit operation in the chemical process industries. As a rule, this process is used for removal or recovery of non-VOC gases and is applied within a chemical process as opposed to end-of-pipe "pollution control." The principal operating difference between these two applications is the absorbate concentration, which is relatively high in chemical processing and relatively low for pollution control. Though no specific example is presented herein for VOC recovery from small industrial sources, there are several texts the reader may wish to consult on the general topic of absorption, including Treybal, [9] Buonicore and Theodore, [7] Crawford, [10] Marchello [11], and Silver and Hopton¹² which provide general design procedures and some specific examples for other applications.

Condensation

Condensation is the simplest of the three VOC recovery techniques. It is a straightforward heat exchange process, which is discussed in numerous standard texts, including Kern [13] and Perry [14].

The governing equation for heat exchange processes can often be reduced to:

$$Q = U A \Delta T \quad (2)$$

where Q = rate of heat transfer, Btu/hr

U = overall heat transfer coefficient,
Btu/hr-ft²-°F

A = heat exchange surface area, ft²

ΔT = log mean temperature difference, °F

Although the above expression is simple, much infor-

mation is needed to design or evaluate a condenser for a specific VOC recovery application. This information includes physical properties of the VOC-containing gas and the coolant as well as the heat exchanger geometry.

Specifically for VOC recovery, the gas stream is usually air and the cooling fluid of economic choice is cooling water. Design inlet temperatures for industrial cooling water, depending on season and location, are usually 80 to 100°F. From the above equation, if the VOC condenses at a temperature less than this, it cannot be recovered by condensation unless another coolant is used. Such coolants and related equipment are readily available, but add to the capital and operating costs.

VOC concentration in the inlet gas is also important. Since the entire gas stream must be cooled to condense the VOC, energy costs can be prohibitive if the VOC concentration is low. Below about 5,000 ppm, recovery by condensation is not usually practical [2], this limit is purely economic, however, because in principle almost any VOC could be recovered from a given inlet gas stream by condensation.

If the dew point of the inlet gas stream is higher than the coolant temperature, water will condense along with the VOC. This can cause two problems, corrosion and low VOC purity. Corrosion will result if the VOC hydrolyzes easily or forms any corrosive compound on contact with water, as some chlorinated VOCs do. If the VOC is water-soluble or toxic, condensation of water simultaneously with the VOC will require subsequent VOC-water separation or wastewater treatment to remove the toxic VOC from any discharged water, respectively. One way to avoid this problem is to use a desiccant bed (molecular sieves, alumina, or silica gel) upstream of the condenser (see Kohl and Reisenfeld [5]).

VOC removal efficiencies by condensation can be fixed at any level desired, the only constraint being cost. If greater than 90% removal must be achieved, coolants other than cooling water must generally be used [2] especially if low-molecular-weight VOCs are present.

For inlet gas streams containing more than one VOC, it is possible, though not normally practical, to design partial condensers in series, each of which condenses one VOC. This could become practical if the VOCs differed widely in boiling points, say by at least 75 to 100°F.

Finally, the condensed VOC may form either an aerosol or entrained droplets in the heat exchanger at practical gas velocities. If either occurs, the VOC must be recovered by either demisters or a collection device such as a cyclone. The overall efficiency of the VOC recovery process (condensation and collection) may be significantly reduced if the aerosol/droplet size is much less than about 5 μ m. Aerosol formation can be minimized by limiting the gas velocity through the condenser.

ECONOMICS

Adsorption

The single most important factor affecting the capital cost of a carbon adsorption system is the volumetric throughput, ft³/min. Typical capital costs for conventional steam-regenerated systems are \$15-20/ft³/min [3]. When the VOC concentration in the inlet gas stream is less than about 300 ppm, one vendor reports the use of a "thin bed" (4 to 18-inch bed depth) to lower this capital cost to about \$10/ft³/min for systems greater than 10,000 ft³/min [3]. The only other capital costs available show that dehumidification to <50% RH may add about \$1/ft³/min to the \$15-20/ft³/min above [3]. One qualitative observation is that the cost of VOC recovery increases very rapidly as the VOC mass flow rate decreases to below 100 lb of VOC/hr [5]. For a VOC of molecular weight 100 at a concentration

of 1,000 ppm, this mass flow rate corresponds to a total gas flow rate of 6,500 ft³/min at 1 atm pressure and 75°F.

Operating costs include steam, electricity, and condenser water for the conventional system considered here. Steam usage is reported to be 0.25 to 0.35 lb steam (at 15 psig)/lb carbon [3] or about 6 lb steam/lb VOC [4]. Electricity usage is about 2.9 to 4.5 kW/1,000 ft³/min [3, 4]. Condenser water is used at about 12 gal/min per 100 lb steam [3]. Replacement carbon, if needed, costs about \$3-6/lb, with a typical carbon life being up to 5 years [3, 4]. This results in carbon replacement costs of roughly \$7 per lb VOC per hr per year [4].

Absorption

Because absorption costs depend strongly on the VOC-absorbent equilibrium relationship, choice of absorbent, and choice of stripping agent, representative economics for VOC recovery from small industrial sources are difficult to determine.

Vatavuk and Neveril have described a procedure to estimate capital and operating costs for absorption processes for pollution control [16]. Zenz gives a detailed design procedure for absorption towers, but does not discuss economics in detail [17]. The reader should also consult Peters and Timmerhaus for absorption equipment costs [6, pp. 768-776].

Condensation

Because condensation is a simple heat transfer process, there are two major capital cost elements the heat exchanger (condenser) itself and the refrigeration unit, if needed. Heat exchanger costs are very modest by comparison to system costs for carbon adsorption. Heat exchanger costs as a function of surface area are given by Peters and Timmerhaus [6, pp. 668-671]. For most VOC recovery applications, the heat exchanger can be made of carbon steel and designed for modest coolant pressures (coolant is usually on the tube side of a shell and tube condenser) and near-atmospheric shell-side pressures. Costs for other materials of construction such as stainless, Monel, or Hastelloy are considerably higher than for carbon steel.

The refrigeration unit cost depends on the heat duty (Btu/hr) and, to a lesser though significant extent, on the

temperature of the coolant at the inlet to the condenser. For typical VOC recovery applications, coolant inlet temperatures of -10 to +10°F are adequate to condense VOCs with boiling points down to about 60 to 80°F.

Operating costs are primarily for electricity, especially if a refrigeration unit is required. Purcell and Shareef (p. 5-27) cite a typical value of 1.5 kW of electricity per ton of refrigeration (1 ton refrigeration = 12,000 btu/hr) [2]. At a cost of \$0.06/kWh and at an annual operating rate of 8,000 hr/yr, annual electrical costs would be:

$$\begin{aligned} \text{Annual electrical costs} &= \left[\frac{1.5 \text{ kW}}{\text{ton}} \right] \left[\frac{\$0.06}{\text{kWh}} \right] \left[\frac{8000 \text{ hr}}{\text{yr}} \right] \\ &= \$720/\text{yr/ton refrigeration.} \end{aligned}$$

Comparison of Technologies

Although it is not within the scope of this article to present detailed specific comparisons of VOC recovery techniques, the results of one such study [8] comparing carbon adsorption and condensation are presented in Table 3.

These results support the general comparisons of Figure 4. Specifically, this study shows that condensation is not economical at low VOC concentration, that condensation is more capital-intensive than adsorption, and that at the highest VOC concentration examined (8,000 ppm), condensation is competitive with adsorption. Also note the two options for use of the recovered VOC—either as a solvent or a fuel. Reuse as a solvent is considerably more economical in all cases. This study also concludes that only carbon adsorption is capable of practical removal efficiencies of 95% or greater (condensation is assumed to achieve 90% typically).

EXAMPLE CASES

Adsorption

The purpose of this section is to provide the reader with an example of the application of the design and technical discussion to a specific case of VOC recovery by activated carbon adsorption.

For any VOC recovery need, the buyer must know or obtain certain information about the VOC-containing gas

TABLE 3. SUMMARY OF COSTS FOR CONDENSATION AND FIXED-BED CARBON ADSORPTION^{a,b}

Stack Gas Emissions Concentration (ppm volume) ^c	Cost Item	Condensation		Fixed-Bed Carbon Adsorption	
		Recovered Solvent Reused	Recovered Solvent Used as Fuel	Recovered Solvent Reused	Recovered Solvent Used as Fuel
200	Total capital cost (\$)	691,600	691,600	140,000	140,000
	Annual direct cost (\$/yr)	-147,600	-161,900	-9,700	-24,700
3,000	Total capital cost (\$)	706,300	706,300	140,000	140,000
	Annual direct cost (\$/yr)	+175,800	-35,200	+228,600	+21,800
8,000	Total capital cost (\$)	613,500	685,700	259,600	259,600
	Annual direct cost (\$/yr)	+687,200	+160,000	+634,800	+91,800

^a Negative annual direct cost indicates expenditure; positive annual direct cost indicates earned revenue.

^b This table is from reference 8, p. 126.

^c The VOC-containing gas stream evaluated is: 5,000 standard ft³/min flow rate, 300°F inlet temperature (this implies the need for precooling for the carbon adsorption case), and 6% RH. The VOC is a complex hydrocarbon mixture assumed to have the empirical formula C₁₀H₂₀.

TABLE 4. INFORMATION NEEDED FOR ADSORPTION SYSTEM DESIGN

Item	Value For Example Case
Flow rate of VOC-containing gas stream	20,000 ft ³ (STP)/min
VOC content of the gas stream	1,200 ppm toluene in air
Gas-stream temperature	110°F
Impurities in the gas stream	dust (trace amount)
Relative humidity of the gas stream	75%
Value of recovered solvent	\$8.86/lb
Available utilities	
Steam	15 psig
Electricity	sufficient (some vendors ask for specific volts, amps)
Cooling water	sufficient (some vendors ask for specific supply temperature, pressure, and even water hardness)
Any space limitations	none
Operating schedule	8,000 hr/yr

stream and the site. Specific values have been selected for the example exercise herein (see Table 4). From this information the buyer can make the following judgments and calculations about the VOC recovery system under consideration.

Gas Conditioning: The gas-stream temperature, relative humidity, and the presence of dust (Table 4) indicate the need for gas conditioning upstream of the carbon beds. This gas conditioning must accomplish particulate removal (via a filter) and cooling/dehumidification to approximately 80 to 100°F and <50% RH (via a condenser/heat exchanger).

Sorbent Bed: The lower explosive limit (LEL) for toluene in air is 12,000 ppm, [2] thus there is no need for dilution of the gas stream for safety reasons because up to 25 to 50% LEL can be tolerated with some special controls. The approximate sorbent bed size can be calculated from the general guidelines discussed earlier of 100 ft³/min superficial velocity and the throughput of 20,000 ft³ (STP)/min at, say, 70°F:

$$\begin{aligned} \text{Carbon bed cross-sectional area} &= \left[\frac{20,000 \text{ ft}^3/\text{min}}{100 \text{ ft/min}} \right] \\ &\quad (460 + 70^\circ\text{R}/492^\circ\text{R}) \\ &= 215 \text{ ft}^2. \end{aligned}$$

From an isotherm of toluene adsorption on one activated carbon, [3] at 70°F and 1,200 ppm in the VOC-containing gas, the "saturation capacity" or *equilibrium* adsorption of toluene is 30% (i.e., 1 lb of this particular carbon will adsorb 0.3 lb of toluene at 70°F at equilibrium). Using an arbitrary conservative value for the "working capacity" of 25% of the saturation capacity for a typical 1-hr on-line cycle [3, 4] the working capacity is:

$$\begin{aligned} \text{Working capacity} &= (0.25) (0.3 \text{ lb toluene/lb carbon}) \\ &= 0.075 \text{ lb toluene/lb carbon}. \end{aligned}$$

For single VOCs other than toluene, the saturation capacity at inlet temperatures of 70 to 90°F, <50% RH, and 300 to 5,000 ppm VOC will vary between roughly 20 and 40 wt percent (i.e., 1 lb carbon will adsorb between 0.2 and 0.4 lb VOC at equilibrium at these conditions). Thus, using 25% of this saturation capacity as the working capacity, a rule of thumb working capacity (in the absence of any other information) would be 5 to 10 wt percent. Be cautioned that it is always better to have experimental data for the VOC of interest, however.

The mass flow rate of toluene is:

Mass flow rate of toluene

$$\begin{aligned} &= \left[\frac{1200 \times 10^{-6} \text{ lb-mole toluene}}{\text{lb-mole gas}} \right] \\ &\quad \left[\frac{92 \text{ lb}}{\text{lb-mole toluene}} \right] \left[\frac{20,000 \text{ ft}^3 (\text{STP})}{\text{min}} \right] \\ &\quad \left[\frac{\text{lb-mole gas}}{359 \text{ ft}^3 (\text{STP})} \right] \left[\frac{60 \text{ min}}{\text{hr}} \right] \\ &= 369 \text{ lb toluene/hr}. \end{aligned}$$

Thus, the actual carbon requirement for a 1-hr cycle time will be:

Actual carbon requirement

$$\begin{aligned} &= \left[\frac{369 \text{ lb toluene}}{\text{hr}} \right] [1 \text{ hr}] \\ &\quad \left[\frac{\text{lb carbon}}{0.075 \text{ lb toluene}} \right] \\ &= 4,920 \text{ lb carbon}. \end{aligned}$$

Knowing that the bulk density of most granular activated carbon is about 30 lb/ft³ and that the bed surface area is 215 ft², then the bed depth is calculated to be

$$\begin{aligned} \text{Bed depth} &= \left[\frac{4,920 \text{ lb carbon}}{30 \text{ lb/ft}^3} \right] \left[\frac{1}{215 \text{ ft}^2} \right] \\ &= 0.76 \text{ ft}. \end{aligned}$$

This bed depth is too shallow to adsorb any but the smallest levels of VOCs (such shallow beds are, however, recommended for VOC concentrations in the range of 10 to 100 ppm [3]). To obtain a more appropriate bed depth of at least 18 inches [3], and preferably 2 to 3 feet, it will be necessary in this example to increase the amount of carbon on-line from 4,920 lb (using a 2-ft bed depth) to:

$$\begin{aligned} \text{Carbon needed on-line at any one time} &= (2 \text{ ft}) (215 \text{ ft}^2) \left[\frac{30 \text{ lb}}{\text{ft}^3} \right] \\ &= 12,900 \text{ lb carbon}. \end{aligned}$$

This would probably be done with a three-vessel system, with each vessel containing 6,450 lb carbon and with two vessels on-line at any one time. Such an arrangement would reduce the total amount of carbon needed from a total of 25,800 lb carbon for a two-bed system (two 12,900-lb beds) to a total of 19,350 lb carbon (three 6,450-lb beds).

The steam usage, based on a 1-hr cycle, will be approximately:

$$\begin{aligned} \text{Steam usage} &= \left[\frac{0.3 \text{ lb steam}}{\text{lb carbon}} \right] \left[\frac{6,450 \text{ lb carbon}}{\text{hr}} \right] \\ &= 1,935 \text{ lb steam/hr}. \end{aligned}$$

The blower horsepower will be:

$$\begin{aligned} \text{Blower hp} &= \left[\frac{6 \text{ hp}}{1,000 \text{ ft}^3/\text{min}} \right] (21,500 \text{ ft}^3/\text{min}) \\ &= 129 \text{ hp}. \end{aligned}$$

VOC Recovery: Because steam is used as the regenerating gas, the VOC recovery section will consist of a condenser and a decanter.

The condenser water needs will be (for a 1-hr cycle):

$$\begin{aligned} \text{Condenser water flow} &= \left[\frac{12 \text{ gal/min}}{100 \text{ lb steam}} \right] (1,935 \text{ lb steam}) \\ &= 232 \text{ gal/min}. \end{aligned}$$

One point of caution is that for this particular case, the aqueous solubility of the VOC in water is negligible. Thus, the VOC can be recovered directly and reused or sold, and the decanted water is probably suitable for

boiler or condenser feed. This may not be true in some applications, and the buyer should be careful that the recovered VOC is not unduly contaminated with water, nor the water with VOC. The presence of such cross-contamination, even at fairly small levels, can drastically affect the economics of VOC recovery.

System Costs: Based on the rough guidance discussed earlier, the capital cost of the entire system rounded to the nearest 100 dollars is about:

$$\begin{aligned}\text{Capital cost} &= \left[\frac{\$20}{\text{ft}^3/\text{min}} \right] (21,500 \text{ ft}^3/\text{min}) \\ &= \$430,000.\end{aligned}$$

Carbon cost (included in the above capital cost) will be (at \$4/lb):

$$\begin{aligned}\text{Carbon cost} &= (\$4/\text{lb})(19,350 \text{ lb carbon}) \\ &= \$77,400.\end{aligned}$$

A 5-year typical carbon life implies a 20%/year carbon replacement cost, or \$15,500/yr.

Annual electrical costs at \$0.06/kWh and 4 kW/1,000 ft³/min and 8,000 hr/yr operation will be:

Annual electricity cost

$$\begin{aligned}&= \left[\frac{8,000 \text{ hr}}{\text{yr}} \right] \left[\frac{\$0.06}{\text{kWh}} \right] \left[\frac{4 \text{ kW}}{1,000 \text{ ft}^3/\text{min}} \right] (21,500 \text{ ft}^3/\text{min}) \\ &= \$41,300.\end{aligned}$$

Annual steam cost (at \$1/1000 lb) will be:

$$\begin{aligned}\text{Annual steam cost} &= \left[\frac{1,935 \text{ lb}}{\text{hr}} \right] \left[\frac{8,000 \text{ hr}}{\text{yr}} \right] \left[\frac{\$1}{1,000 \text{ lb}} \right] \\ &= \$15,500.\end{aligned}$$

Annual condenser water cost (at \$0.15/1000 gal) will be:

Annual condenser water cost

$$\begin{aligned}&= \left[\frac{232 \text{ gal}}{\text{min}} \right] \left[\frac{60 \text{ min}}{\text{hr}} \right] \left[\frac{8000 \text{ hr}}{\text{yr}} \right] \left[\frac{\$0.15}{1000 \text{ gal}} \right] \\ &= \$16,700.\end{aligned}$$

There will be a credit for the recovered VOC as well. Assuming 95% overall efficiency and a value of \$8.86/100 lb for toluene, [6] this annual credit will be:

$$\begin{aligned}\text{VOC recovery credit} &= \left[\frac{\$8.86}{100 \text{ lb}} \right] [0.95] \\ &\quad \left[\frac{369 \text{ lb}}{\text{hr}} \right] \left[\frac{8,000 \text{ hr}}{\text{yr}} \right] \\ &= \$248,500.\end{aligned}$$

In summary for this case, the costs will be roughly:

Capital cost	\$448,000
Annual operating cost	
Carbon replacement	15,500
Electricity	41,300
Steam	15,500
Condenser water	16,700
Annual operating credit	\$248,500.

To the annual operating costs must be added direct and indirect labor and related indirect annual expenses (taxes, insurance, etc.). The capital cost must be amortized and a

final cost (or credit) in \$/yr determined. This exercise is specific to each small industrial user and is not completed herein. However, the above should provide the user with a starting point for such an evaluation.

Condensation

The following example is summarized from Purcell and Shareef [2, pp. 4.7-1f] and demonstrates the condensation of a VOC from a gas stream typical of one to which this technique can be applied—relatively low flow rate and high VOC concentration.

For this case, we assume the following:

Inlet gas flow rate	2,000 actual ft ³ /min
Inlet gas temperature	90°F
VOC	styrene
VOC concentration	13,000 ppm
Moisture content	negligible***
Condenser operating pressure	1 atm
Removal efficiency required	90%.

The key variable above is the required removal efficiency. To achieve 90% removal (i.e., an outlet concentration of 1,300 ppm), the temperature of the gas stream must be reduced at least below that at which the equilibrium vapor pressure of styrene in air at 1 atm is (1,300 × 10⁻⁶)(760 mm Hg), or 1.0 mm Hg. This temperature is 20°F for styrene. (In general, knowledge of the equilibrium vapor pressure-temperature behavior for the VOC(s) of interest is required.)

Because a coolant temperature of at most 20°F is needed, refrigerated coolant fluid is used. This is usually a "brine" solution, which can be simply water with an appropriate antifreeze added (CaCl₂ is selected for the example case [2]).

The condenser heat load is calculated by a straightforward heat balance on the inlet and exit gas:

$$\begin{aligned}\text{Condenser heat load} &= 241,000 \text{ Btu/hr.}\end{aligned}$$

The condenser surface area is given by the basic design equation $Q = U A \Delta T$. The log mean ΔT can be calculated by specifying, somewhat arbitrarily, an "approach" temperature of 15 to 25°F, meaning that the outlet gas temperature is specified to be 15 to 25°F higher than the coolant temperature at the condenser outlet. Using an approach of 15°F and specifying that the coolant temperature rise be limited to 25°F (this may be limited by the refrigeration equipment), and further assuming the inlet coolant temperature to be 5°F, ΔT is

$$\begin{aligned}\Delta T &= \frac{(90^\circ - 30^\circ\text{F}) - (20^\circ - 5^\circ\text{F})}{\ln [(90^\circ - 30^\circ\text{F})/(20^\circ - 5^\circ\text{F})]} \\ &= 32^\circ\text{F}.\end{aligned}$$

Calculation of U , the overall heat transfer coefficient, can be an extremely time-consuming process, but is nevertheless necessary. Unfortunately, some shortcut methods can result in considerable error, and the reader is urged to go through the procedure of Kern [13] or others to obtain a reasonable value. Purcell and Shareef² use a value of 20 Btu/hr-ft² · °F as "conservatively assumed" and cite Ludwig [15] as a reference. Using this value, the heat exchanger area is:

$$\begin{aligned}A &= Q/U \Delta T \\ &= \frac{(241,000 \text{ Btu/hr})}{(20 \text{ Btu/hr-ft}^2\text{-}^\circ\text{F})(32^\circ\text{F})} \\ &= 377 \text{ ft}^2.\end{aligned}$$

***If the dewpoint of the inlet gas were close to the dewpoint of the VOC, then a desiccant might be necessary upstream of the condenser.

The coolant flow rate, after calculating a coolant heat capacity of 0.65 Btu/lb-°F and recalling the specified temperature rise of 5°F to 30°F, is:

Coolant flow rate

$$= \left[\frac{241,000 \text{ Btu}}{\text{hr}} \right] \left[\frac{\text{lb-}^\circ\text{F}}{0.65 \text{ Btu}} \right] \left[\frac{1}{30^\circ\text{F}-5^\circ\text{F}} \right]$$

$$= 14,800 \text{ lb/hr.}$$

The amount of styrene recovered at 90% efficiency will be:

$$\text{Amount of styrene recovered} = (0.90) \left[\frac{2000 \text{ ft}^3}{\text{min}} \right] \left[\frac{\text{lb-mole gas}}{359 \text{ ft}^3 (\text{STP})} \right]$$

$$\left[\frac{13,000 \times 10^{-6} \text{ lb-mole styrene}}{\text{lb-mole gas}} \right]$$

$$\left[\frac{104 \text{ lb styrene}}{\text{lb-mole styrene}} \right] \left[\frac{60 \text{ min}}{\text{hr}} \right]$$

$$\left[\frac{492^\circ\text{R}}{460 + 90^\circ\text{R}} \right]$$

$$= 364 \text{ lb styrene/hr.}$$

The purchased equipment cost of a carbon steel shell and tube condenser can be found to be about (see reference [6], p. 670):

$$\text{Purchase cost} = \$8,000.$$

of condenser

To this must be added direct cost and indirect installation costs, which are roughly 120% of the condenser, [16] to obtain the total capital cost of the condenser of about \$17,600. From Peters and Timmerhaus [6, p. 886], the purchased equipment cost of the refrigeration unit is about \$80,000. Assuming the same installation costs of 120%, the refrigeration unit capital cost will be \$176,000, or 10 times that of the heat exchanger.

A major operating cost is electricity for the refrigeration unit and cooling water pumps. Electricity for refrigeration can be estimated assuming 8,000 hr/yr operation and \$0.06/kWh (using a value of 1.5 kW per ton of refrigeration [2] with 1 ton refrigeration equal to 12,000 Btu/hr) to be:

$$\text{Electrical costs} = \left[\frac{\$0.06}{\text{kWh}} \right] \left[\frac{8,000 \text{ hr}}{\text{yr}} \right] \left[\frac{241,000 \text{ Btu}}{\text{hr}} \right]$$

$$\left[\frac{\text{hr-ton}}{12,000 \text{ Btu}} \right] \left[\frac{1.5 \text{ kW}}{\text{ton}} \right]$$

$$= \$14,500/\text{yr.}$$

This may be a significant cost, and it points out the economic reasons for judicious use of condensation as a VOC recovery technique. The reader should also refer to Chandrasekhar and Poulin ([8], p. 126) where a similar conclusion is implied.

ACKNOWLEDGEMENT

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Schechter of the Division of Environmental Management.

NOTATION

Readers more familiar with SI units can convert from units used in the text using the following:

$$0.0283 (\text{ft}^3/\text{min}) = \text{m}^3/\text{min}$$

$$6.87 (\text{psi}) = \text{kPa}$$

$$0.454 (\text{lb}) = \text{kg}$$

$$273 + 5/9 (^\circ\text{F}-32) = ^\circ\text{K}$$

$$2.32 (\text{Btu/lb}) = \text{J/g}$$

$$0.305 (\text{ft/min}) = \text{m/min}$$

$$0.249 (\text{in H}_2\text{O}) = \text{kPa}$$

$$0.293 (\text{Btu/hr}) = \text{W}$$

$$5.68 \times 10^{-4} (\text{Btu/hr-ft}^2-^\circ\text{F}) = \text{W/cm}^2 - ^\circ\text{K}$$

$$0.0929 (\text{ft}^2) = \text{m}^2$$

$$1.01 \times 10^5 (\text{atm}) = \text{kPa}$$

$$0.00379 (\text{gal/min}) = \text{m}^3/\text{min}$$

$$3024 (\text{ton refrigeration}) = \text{kcal}$$

$$\text{Btu/lb} - ^\circ\text{F} = \text{cal/gm} - ^\circ\text{K}$$

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Stringfellow Leachate Treatment with RBC

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A study was conducted with a rotating biological contactor (RBC) for treatment of leachate from the Stringfellow hazardous waste site in Riverside County, California. The leachate was transported from California to Cincinnati, where a pilot sized RBC was installed at the U.S. EPA's Testing and Evaluation (T&E) Facility.

A series of kinetic runs were made with primary effluent from the City of Cincinnati's Mill Creek Sewage Treatment Plant to develop a biomass on the disks and to obtain a standard kinetic removal rate. These runs were then followed with Stringfellow leachate experiments that included

- *Operations at various ratios of leachate to primary effluent*
- *Operations at 100% leachate*
- *Operations to increase the percentage removal of dissolved organics*

This paper reports on the results from these experiments and the effectiveness of an RBC to adequately treat leachate from the Stringfellow hazardous waste site.

INTRODUCTION

Stringfellow is a hazardous waste site that is located in Glen Avon, California which is near Riverside, California. The leachate is generated at an approximate rate of 96 m³/d (25000 gal/d) and contains high concentrations of metals and organics. A leachate treatment facility operates at the site and includes lime treatment for metals removal, followed by clarification, sand filtration, and granular carbon treatment. The effluent from the carbon beds is then trucked 19 km (12 mi) to an Orange County interceptor sewer for disposal.

PROJECT DESCRIPTION

A pilot sized RBC was installed at the EPA Testing and Evaluation Facility (T&E) in Cincinnati for evaluating the biochemical treatability of Stringfellow leachate. The pilot sized RBC contains 1000 m³ (11000 sq ft) of surface area which is approximately 10% of a full-scale RBC. The diameter of the pilot unit is 3.6 m (12 ft), which is identical to a full scale RBC. The length is less than 1 m (3.3 ft), whereas a full scale RBC is 7.6 m (25 ft). The Cincinnati treatment plant's primary effluent (PE) was used to develop a biological population and to obtain basic kinetic data. The ideal condition would have involved using Stringfellow leachate to develop an indigenous biomass. However, the logistics favored the treatment plants PE due to the vast distance between Cincinnati and Riverside, CA. There were plus factors associated with conducting the experiment in Cincinnati, such as the auxiliary support available for installation, chemical analyses, 24 hour monitoring, and biochemical expertise for consultation. The RBC facility was designed to operate in a

batch mode with the 5000 gallons of leachate that was trucked from California to Cincinnati for experimentation. The leachate was lime treated at Stringfellow for metals reduction so that the experiments could concentrate on soluble organics removal with the RBC treatment. The experiments were designed to operate in a batch mode for the following reasons:

- eliminate flow controls
- minimize spillages
- minimize accidental releases into the T&E sewer systems
- improve mass balance analyses
- obtain reaction kinetics data
- control final disposal
- avoid overloading of the shaft
- can be directly scaled for the Stringfellow Site

OBJECTIVE

The prime objective of this project was to determine whether the Stringfellow leachate can be economically converted into an innocuous waste by biochemical treatment with a rotating biological contactor.

Methodology

The RBC was operated with primary effluent supplied from the Metropolitan Sewer Districts of Greater Cincinnati (MSDGC) Mill Creek Treatment Plant (MCTP) to develop an adequate biomass on the RBC disks in preparation for leachate treatment.

The first experimental batches were made with increasing ratios of leachate/RBC treated primary effluent to

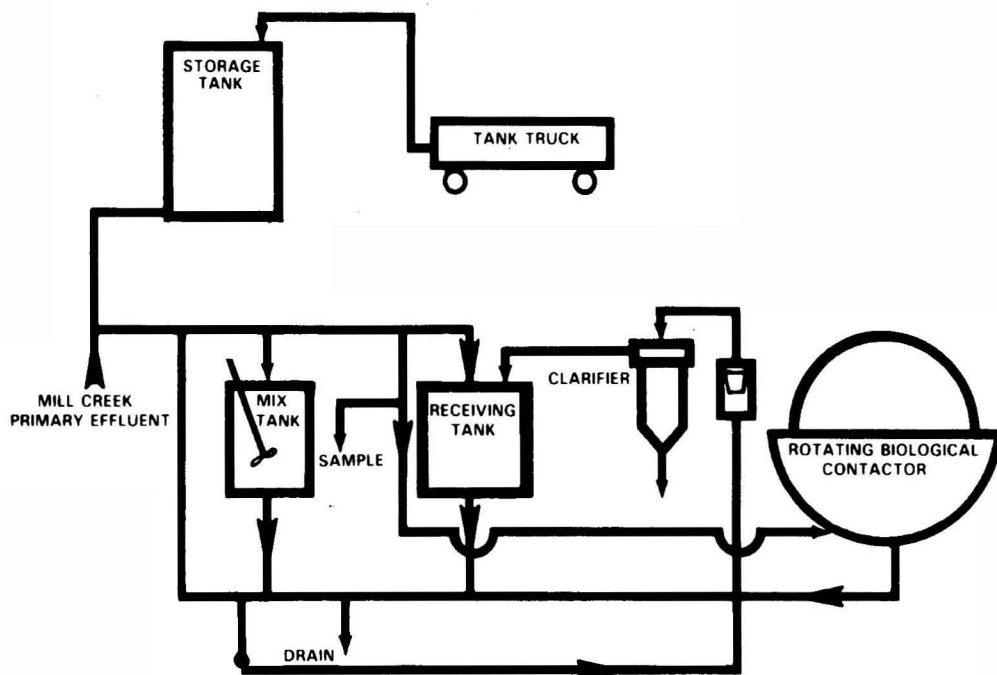


Figure 1. Stringfellow-RBC flow schematic.

allow a gradual acclimation period of the biomass to the leachate. Following these batches the runs were made with 100% leachate. The operation consisted of transferring the leachate from the storage tank to the mix tank where the volume was determined. It was then pumped to the RBC as shown in Figure 1. The RBC was operated at a speed of 1.5 rpm and the operation continued until the dissolved organic carbon (DOC) reached a constant level. The RBC contents were then returned to the mix tank for additional treatment with activated powdered carbon (APC) followed by clarification with ferric chloride to achieve the effluent standards required for disposal to the MCTP. The effluent limitations set by the MSD were: Total organic halides (TOX) < 5 mg/L; vapor space organics (VSO) < 300 ppm; $6 < \text{pH} < 10$.

Internal limits were also set on gross organics that were equivalent to a relatively high strength raw wastewater. These limits were: soluble biochemical oxygen demand, SBOD < 100 mg/L; dissolved organic carbon, DOC, < 100 mg/L; soluble chemical oxygen demand, SCOD, < 300 mg/L.

During the experiment the following parameters were monitored or recorded: Volume of leachate in the RBC; temperature, every 2 hours; speed of rotation, every 6 hours; visual comments on thickness and color of biomass, every 2 hours; dissolved oxygen, every 2 hours; pH, every 2 hours (adjusted with sodium hydroxide when necessary to maintain the pH above 6).

Kinetic Parameters

During the experiment, samples were obtained from the RBC tank at specified time intervals to determine the disappearance of the soluble gross organics. The soluble material is defined as the liquid phase that passes through a Whatman 934AH filter. The gross organics monitored included SBOD, DOC, and SCOD. During each exper-

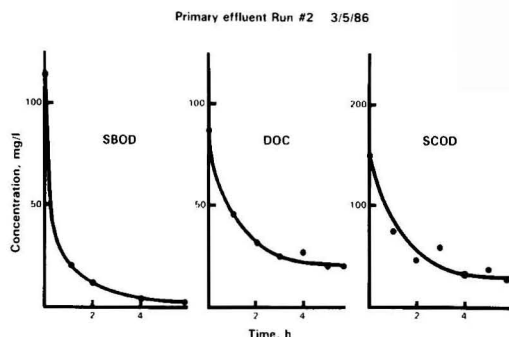


Figure 2. Disappearance of soluble gross organics with time.

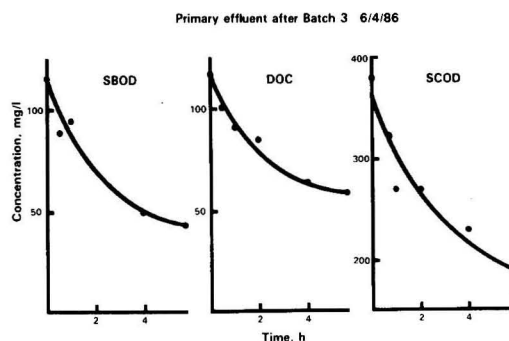


Figure 3. Disappearance of soluble gross organics with time.

TABLE 1. SOLUBLE GROSS ORGANICS REMOVAL FOR PE
Six Hour Residence Time

Date	SBOD, mg/L		DOC, mg/L		SCOD, mg/L	
	In	Out	In	Out	In	Out
6/20	77	0.94	85	20	340	54
6/19	99	0.00	74	10	310	20
6/18	72	0.8	70	13	300	27
6/16	55	1.3	57	11	210	41

iment the DOC was determined on site to obtain information on the progress of the reaction.

In addition to the gross organics, the raw leachate and the treated effluent were analyzed for: suspended solids, (SS); volatile suspended solids, (VSS); nitrogen series, including Kjeldahl, ammonia, nitrite, and nitrates phosphorus, (P); and specific organic contaminants; para-chlorobenzene sulfonic acid (CBSA); 1,2 dichlorobenzene; o-xylene; chloroform; ethylbenzene; 2-hexanone; tetra-chloroethylene.

RESULTS AND DISCUSSION

The rate of soluble organic removals was determined for the Mill Creek primary effluent by following the disappearance of SBOD, SCOD and DOC with time. A typical curve for the disappearance of soluble organics using

PE is displayed in Figure 2 and this curve is used as a base for comparison with PE following experiments with leachate on the RBC. The removal rate is typical for PE which can best be described as a high rate process as indicated by the rapid dropoff in gross organics after two hours of reaction time.

After three experiments with diluted leachate, there occurred a slough off of biomass from the disks as witnessed by an increase of solids in the RBC tank. It was questionable as to whether sufficient biomass was present on the disks, therefore the leachate was replaced with PE and an experiment was conducted to obtain the rate of disappearance of soluble organics with time. The curve in Figure 3 represents the reduction of soluble organics with time for PE. The curve differs considerably from the rapid removal rate experienced with PE in Figure 2. It does not show the initial rapid drop-off of organics or the low residual organics that were previously obtained with PE, indicating that the RBC may have become biomass limited. To correct this situation the biomass was rebuilt using primary effluent with batch times of six hours and again the removals returned to the rapid rate with a relatively low residual as shown in Table 1.

BIOMASS ACCLIMATION

Since the biomass established on the RBC disks was developed with primary effluent, acclimation runs were made to avoid shock loading the biomass with the Stringfellow leachate. The leachate was three to four times stronger in organic concentration than the PE and contained a significant quantity of p-chlorobenzene sulfonic acid, a compound that is foreign to the biomass. The acclimation period consisted of three runs using progressively stronger concentrations of leachate as shown below. The ratio of leachate to PE were:

- Batch #1: Leachate/treated PE = 1/2
- Batch #2: Leachate/treated batch #1 = 1/1
- Batch #3: Leachate/treated batch #2 = 3/1

When leachate was combined with treated PE in batch #1 there were six passive days before the DOC began

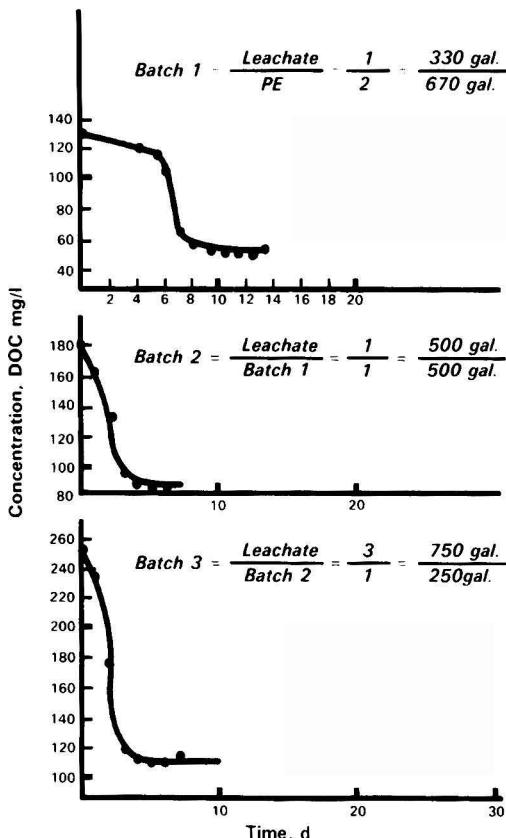


Figure 4. Disappearance of DOC with time using various ratios of leachate to treated effluent.

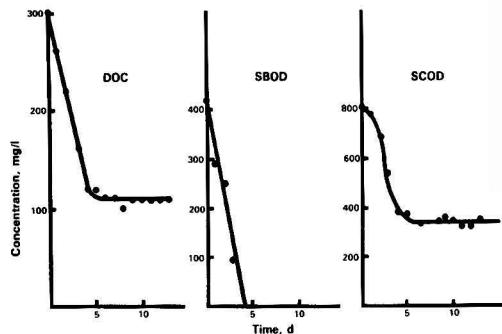


Figure 5. Disappearance of soluble organics with time.

to disappear. After the incubation period the reaction required approximately 2 days to obtain a drop of approximately 60% in the DOC. The residual DOC, approximately 50 mg/L, remained unchanged during an additional 6 days of treatment. This is illustrated in Figure 4 in which the concentration of DOC is plotted against time for the first three batches.

In batch #2 the reaction for the disappearance of DOC began after the first day and was essentially complete after three days. The percent removal of DOC was approximately 50% and the residual DOC was approximately 90 mg/L. The result for batch #3 was similar to batch #2. That is, after a passive 24 hours, the reduction in DOC was essentially complete after three days. The DOC removal was approximately 55% and the batch had a final DOC of 120 mg/L.

Batch #3 was continued for an additional 27 days to determine if an extended time period would result in a further reduction in DOC. The additional time had no effect on DOC as shown in Figure 4.

100% LEACHATE OPERATION

Following the acclimation runs, where increasing concentrations of leachate were used to gradually expose the biomass to the leachate, the next two runs used 100% leachate.

The results were similar to those obtained during the acclimation runs 2 and 3. A plot of the soluble organics removal versus time for SBOD, DOC and SCOD is shown in Figure 5. We conclude from this data that: approximately four days were required to reduce the DOC from 300 to 100 mg/L. This closely approximates the results obtained with the leachate and PE mixture and is in contrast to only 2 hours that is needed to obtain a large DOC reduction with PE.

The removal rate is significantly below the rate obtained with PE. Previous work on RBC's showed a SBOD removal rate of 440 mg/h·m² (40 mg/h·ft²) with municipal wastewater; whereas the leachate gave 19 mg/h·m² (1.7 mg/h·ft²).

The RBC operation required pH adjustment. As the DOC dropped during the reaction phase the pH would fall and require periodic additions of sodium hydroxide to maintain a pH greater than six.

Sodium phosphate was added to the leachate to provide adequate levels of P to maintain a satisfactory supply of nutrients. Characterization of the leachate indicated that

nitrogen was readily available as nitrate and therefore no adjustment was needed in regard to nitrogen.

The major identified organic constituent, p-chlorobenzene sulfonic acid was readily removed during RBC treatment. The 35% DOC that was not removed during the RBC treatment was not identified by a GS-MS scan, because of the nature of the compound/compounds.

The leachate final concentrations were

110 mg/L for DOC

1 mg/L for SBOD

370 mg/L for SCOD

These results showed close to 100% removal for biodegradable organics as defined by SBOD. They also showed that a significant fraction of refractory organics remained after the treatment. In the case of DOC only 63% was removed and only 54% of the SCOD was removed.

In order to meet the limits specified for disposal into the Mill Creek Wastewater Treatment Plant, it was necessary to treat the leachate with activated powdered carbon to remove additional refractory organics. The RBC contents were transferred to a mix tank where 12 to 15 grams of activated carbon per gram of DOC were added. Separation of the carbon from the leachate was achieved by flocculation with ferric chloride during clarification. The previously specified limits were met:

- TOX was under 5 mg/l
- DOC = 20 mg/l
- SCOD = 79 mg/l

The results from the treatment of leachate with an RBC, followed by activated powdered carbon and clarification with ferric chloride is shown in Table 2.

ECONOMIC EVALUATION

The process used at Stringfellow employs regenerated activated granular carbon for removing the soluble organics from the leachate. The cost for regenerated activated granular carbon is \$290,000 per year based on the following factors: A leachate treatment rate of 96 m³/d (25000 gal/d); average TOC inlet concentration of 350 mg/L; effluent TOC concentration of 30 mg/L; carbon usage is 0.35L leachate/g (41 gal/lb C); carbon dosage is 8.2 g C/g DOC. The cost of regenerated carbon is \$2.86/kg (\$1.29/lb).

The savings per year that can be realized by treating the leachate with an RBC is estimated at \$190,000 through savings in carbon costs. These savings are offset by the RBC capital costs which are estimated at \$630,000 based on the results obtained at the pilot plant. Nine RBC's are required to satisfy the 4 days of reaction time determined in the pilot plant study. The estimated installed cost is \$630,000. Approximately 3.3 years of operation will be required to recover the capital expenditures for the proposed RBC's.

However the RBC is capable of removing the equivalent of 440 mg/h·m² (40 mg/h·ft²) SBOD in one hour when operating on primary effluent. When operating on Stringfellow leachate, the RBC removed only 19 mg/h·m² (1.7 mg/h·ft²) of SBOD in one hour indicating that the biomass may only be 10% acclimated; thus causing the low reaction rate. A study on site is recommended to determine whether a day to day operation with leachate using a full scale RBC could reduce the reaction time. This would provide a biomass that was indigenous to the leachate and possibly yield a reaction rate that was significantly faster than the rate obtained during these experiments.

The biochemical kinetics for Stringfellow leachate is less than 10% of the specific reaction rate for primary effluent, and may be attributed to the reaction rates of the specific chemicals involved in the biodegradation reaction.

TABLE 2. TREATMENT OF 100% STRINGFELLOW LEACHATE

	Leachate mg/L	RBC Effluent, mg/L	APC + Clarification Effluent mg/L
SBOD	420	0.0	0.9
BOD	440		2.2
DOC	300	110	20
TOC	310		22
SCOD	800	360	79
COD	840		95
SS	43		23
VSS	31		14
TKN	6.3		7.5
NH ₃ -N	3.4		6.3
NO ₃ -N	44		34
NO ₂ -N	ND*		ND*
P	3.5		2.3

* Not detected.

The scaleup for Stringfellow is based on providing sufficient time of reaction, 4 days, by installing nine standard size RBC's, which contain 45 m^3 (12000 gal) of leachate based on $.0049 \text{ m}^3/\text{m}^2$ ($0.12 \text{ gal}/\text{ft}^2$) of surface area, or 410 m^3 (108,000 gal) total. Four days of leachate generation averages 380 m^3 (100,000 gal). If we assume the worse condition, and that is, the specific reaction rate is less than 10% of the rate for PE, then a standard size RBC may have adequate biomass present on its 100,000 square feet of surface area. We can assume the oxygen transfer rate as equivalent to the rate obtained with primary effluent when the speeds of rotation are the same, 1.5 rpm, and therefore more than adequate for satisfying the leachate requirements. Then the biochemical reaction can be assumed to be reaction rate limited and a modification to the RBC is proposed that would decrease the number of RBC's from nine to two. The tankage for each of the two proposed RBC's would be increased from 45 m^3 (12000 gal) to 280 m^3 (75000 gal) each to take into consideration adequate reaction time, fill time, and drain time. This approach would provide enough volume to satisfy the reaction time of 4 days and yet it would contain only 9300 m^2 (100,000 ft^2) of surface area for each of the two RBC's. There should be sufficient disk area and oxygen transfer capability to satisfy the reaction rate required for Stringfellow leachate. This equipment modification would reduce the capital costs from \$630,000 to \$200,000 and cut the capital recovery time from 3.3 years to 1.1 years. This design approach increases the attractiveness of the cost savings that can be realized by installing RBC's at Stringfellow.

The study on treating Stringfellow leachate with a RBC showed that: 65% of the dissolved organic carbon can be removed by biological treatment. The residuals remaining after biological treatment will require further processing with activated carbon to achieve levels below 100 mg DOC/L . The direct scaleup of the pilot plant result to the Stringfellow site would require 3.3 years of operation to recover the capital costs for a RBC treatment stage. A modified design scaleup based on satisfying the reaction time requirements is an attractive alternative to reduce capital costs and thus reduce the capital cost recovery period from 3.3 years to 1.1 years.

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Environmental Review Strategy for R&D Activities

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An organized environmental review strategy can assist an R&D facility or organization in ensuring that their activities not only comply with applicable site and operational requirements, but also address and resolve environmental issues and costs during the process development phase of their work. It is at this stage of R&D where efforts toward minimizing generation of hazardous waste and reducing "end-of-the-pipe" control in potential commercial applications can be most effective. This article presents and describes five basic concepts which, when combined, can create a strong, purposeful environmental review program. Exxon Research and Engineering Company's review process is described as a specific example.

INTRODUCTION

Environmental awareness, regulatory interaction, and media attention usually associated with process plants is now also being applied to research and development activities. An organized environmental review strategy can ensure these activities not only comply with pertinent site and operational requirements, but also address and resolve environmental issues and costs during process development so as to minimize waste generation and reduce "end-of-the-pipe" control methods in potential commercial applications. Basic concepts of an environmental review strategy for organizations to use in creating review programs for their research and development activities is presented here. Exxon Research and Engineering Company's review process is described as a specific example.

Basic Strategy Concept

Environmental review programs can exist in a variety of forms and may include a diversity of procedural steps. Most, however, seem to be based on five basic strategy concepts:

- 1) Provide management support
- 2) Include individual researchers and engineers
- 3) Review diverse areas of environmental concern
- 4) Conduct reviews with knowledgeable persons
- 5) Include a recognition system

Each of these is discussed in more detail below.

Provide management support during and after the introduction program. An introductory letter signed by the

organization's president or laboratory director can be a very powerful message of support. The company environmental manager might also be a co-signer. This letter can be distributed by "desk-top" distribution, company mail, or work group meetings. Attaching a brochure or a similar attachment describing the program, procedure, and form completes the program introduction.

However, unless the support continues after this introduction, few if any benefits will be realized. Division managers, supervisors, and others must make time allowances for personnel to consider review questions, obtain unknown and/or necessary information, and participate in the review discussions. Unique and innovative ideas which otherwise might not have been raised, frequently emerge from such activities.

The introduction of a review program such as this is facilitated if it can be incorporated into an existing review process. Are the activities currently reviewed for budgetary, safety, or industrial hygiene aspects? Why not include an environmental review in the process?

Include individual researchers, engineers, and scientists in the review, even to the extent of being responsible for its completion. This creates a sense of "ownership" and increased pride, particularly for any resultant successes. The review process has the potential to stress both company and individual responsibilities in the advancement of environmentally sound processes. Eventually it can be accepted as an everyday part of their normal R&D activity.

Review diverse areas of environmental concern during the review, rather than limiting it to one aspect. As long as environmental issues are being addressed, look at air pollutant emissions, wastewater discharges, and spill prevention and control. Also, review the types of waste being generated, their amounts, and their hazardous characteristics. A multi-media approach can identify a variety of needs, such as:

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- Are any air emission permits required?
- Is there a suitable disposal plan for spent scrubber solution? Is there an alternative?
- Can the site or public wastewater treatment plant handle the amount and quality of process water?
- How can the volume or hazardous nature of the wastes be reduced or eliminated?

Of course, information on the unit description, process, and location will be required. The person desiring to conduct the research or development should be able, and responsible, for supplying most of the information. Design and construction personnel may be able to supply other important information. Frequently, only basic process information will be available at first, since definition and variability of the process is often the subject of the research!

Conduct reviews with personnel knowledgeable both in technical processes as well as environmental issues and regulations. It may be difficult to have a person on the staff with experience in both areas, but if available, he or she can provide valuable insight into previously encountered solutions and results. If on-site environmental expertise is unavailable, an outside consultant may be useful in certain circumstances, though a confidentiality agreement may be required.

Include a recognition system for innovative designs or ideas. The recognition can be financial, company publicity, or other "extra". It could be presented for initial concepts, successful implementation, or even graduated steps between the two. The point is to have a clearly recognizable environmental achievement reward which is noted within a short time frame.

Several companies have formalized the recognition system. The 3M company has sponsored an internal "Pollution Prevention Pays" (3P) program since 1975 to recognize projects which prevent pollution at the source [1]. Individuals whose projects reduce pollution and create monetary benefit receive framed certificates along with special letters of commendation, with copies to their immediate supervisors and division manager or vice president. Those whose projects are also innovative or involve a significant technical accomplishment receive a plaque signed by the company chairman and the staff vice president of the environmental group.

Benefits

It is important to keep in mind during the reviews that functional research and environmental considerations are not mutually exclusive. Even though an investment of time and money may be included, benefits can always be realized. 3M has approved more than 1900 3P projects, saving more than \$328 million worldwide.

A prime example of the benefit of environmental review can be found in the manufacture of titanium dioxide for the coatings industry [2]. A national company, as well as other companies in that industry, was faced with plant closure due to particulate emissions from the existing batch process used throughout the industry. Rather than closing the plant or adding control equipment, a more productive, continuous process was developed which met emission standards without the control device that had been considered necessary. Particulate and SO₂ emissions were reduced 99.6%, energy costs were reduced 25%, and acid wastes were reduced 40%. As a result, not only did the personnel who developed the new process receive extensive acclaim within their industry [3], but the process has become a new industry standard, providing the company with licensing royalties. These savings and rewards might have begun even earlier if the

review were conducted as a part of a regular research and development environmental review program.

The ER&E Experimental Unit Review Program

Exxon Research and Engineering Company's experimental unit review program is being geared toward maintaining on-site compliance as well as improving processes to reduce or eliminate "end-of-the-pipe" pollutant control in commercial units. It is not yet quite as formal as the 3M program, though it also includes safety and industrial hygiene issues. Our program's administrative review procedure and the associated review form is described below as a starting point for others to develop a program suitable for their organization.

The administrative procedure for implementing our review program is conducted through the planning and budget function of our Facilities Engineering Division (FED), which designs and builds experimental units. As shown in Figure 1, the review process is being tied integrally into the pre-existing process of developing a unit's construction schedule and budget estimates.

Review forms are completed by the engineer, or scientist, then reviewed by company environmental, safety, and industrial hygiene staff. If necessary, review sessions are held between staff personnel, the researcher, and the unit design engineer to determine site compliance needs and investigate potential environmental improvements. Release of the final project construction estimate and schedule may be subject to completion of the review.

The Experimental Unit Review Form, shown as Figure 2, solicits the information on the unit, the process and its location. Additional information is requested on process materials, emissions, and current plans on waste handling and minimization. Often at least portions of this information becomes available and subject to discussion only through such a review process. This form generates the information company environmental staff and the researcher need to know to protect personnel and the company facility. Also, it fosters ideas on how to improve the environmental aspects of the unit's design or operation for future commercial development. Reductions in waste generation can have dramatic, positive impacts on company or plant operating costs especially with hazardous waste disposal costs increasing on the order of 50-100% per year.

The ultimate goal of this program is to identify and address environmental impacts and costs at the source as early in the research and development as possible. For example, at one of our sites participation in this review identified the need for several state air pollutant emission permits which, given the lead time provided by the review, were obtained without project delay. Also, a process change which incorporated vapor purification and condensing equipment significantly reduced solvent feedstock and hazardous waste disposal costs.

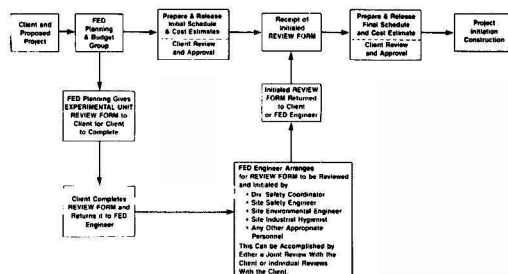


Figure 1. Flow plan for experimental unit review form.

EXPERIMENTAL UNIT REVIEW FORM

THIS REVIEW FORM CONTAINS PROPRIETARY COMPANY INFORMATION. ☐ Yes ☐ No

A. Purpose

This experimental unit review has been developed to solicit information from the researcher regarding the safety, health and environmental aspects associated with a new or modified experimental bench scale engineering prototype, or pilot unit. The research professional should complete the requested information and obtain the required review prior to the Preconstruction Safety Review. This will ensure that a safe, environmentally acceptable unit will be designed, constructed and operated while maintaining a timely schedule. If you require assistance in completing this form, contact your Laboratory or Division Safety Coordinator.

B. Unit Information and Description

Unit Name: _____ Location (Proposed): _____

Unit Status: ☐ New ☐ Modification of Existing Unit ☐ Relocation of Existing Unit

Technical Contact Name: _____ Location: _____ Site _____
Bldg. _____ Tele. No.: _____
Room _____

Laboratory/division: _____ Project No.: _____ Div/Sec No.: _____

Unit Operation (check appropriate boxes): ☐ attended ☐ on-hours ☐ batch
☐ unattended ☐ off-hours ☐ continuous

Unit Run Length: _____ Unit Run Frequency: _____

Project Duration (estimate): _____

Process Description: _____

Key Reaction Parameters/Equations (indicate whether exo- or endothermic and amount):

Simplified Schematic Flow Diagram (label streams and provide flow rates (lbs/hr or kg/hr), pressures (psia or kpa) and temperatures (°F or °C) to the extent possible:

(Part 1 of 4E-82-84)

C. Properties of Materials Used in Unit Operation

Indicate which materials are to be used or found in the given types of streams. (If data are not available, indicate by N.A.)

Materials Code Number: 1-Feeds; 2-Catalysts; 3-Products; 4-By-Products; 5-Wastes; 6-Other.

[illegible]

(1) Physical State Key Code
S = solid G = gas
L = liquid M = mixture

(2) Hazard Code (including impurities or contaminants):
 A = acid B = base C = carcinogen
 COR = corrosive CR = cryogenic F = flammable
 O = oxidizer P = pyrophoric R = reducer
 T = toxic Z = other

(3) TLV = Threshold Limit Value
OEL = Occupational Exposure Limit

D. Physical Agents

Please describe and quantify any of the following physical agents which may affect personnel or the design or use of this unit.

Physical Agent Code Number: 1-Noise; 2-Temperature (heat or cold); 3-Ionizing Radiation; 4-Lasers; 5-Radio Frequency or Microwaves; 6-Electricity; 7-Other.

Physical Agent Code Number	Description of Potential Problem

E. Environmental Concerns

Will there be any potential for:	Yes/No	Material(s)	Maximum Emission Rate	
			per hour	per day
• air pollutant emissions? (includes use of vent lines)	_____	_____	_____ (lbs)	_____ (lbs)
• wastewater discharge? (includes overflow or release to sewer)	_____	_____	_____ (gal)	_____ (gal)
• ground/soil contamination? (includes spill during operation or material handling)	_____	_____	_____	_____

Are there any emission control devices anticipated in the unit's design?

☐ exhaust filters ☐ cyclones ☐ scrubbers ☐ other emission control devices?

If so, describe: _____

E. Environmental Concerns continued

Describe how wastes (unused feeds, samples and products) will be handled and volume/hazard minimized.

F. Other Concerns

Are there any other safety, health, environmental, fire or human factor concerns associated with this unit that have not been addressed on this form?

G. Form Completion and Review

Form completed by: _____

Completed form sent to:

Division/laboratory Safety Coordinator :

Site Safety Engineer :

Site RTSD Pilot Plant Safety/Operations Contact
or EETD Pilot Plant Operations Contact :

Site Environmental Engineer :

Site Industrial Hygienist :

Note to Form recipients: Please notify _____ by phone
no later than ten (10) working days of Form completion date if you wish to attend safety re-
views of the proposed project.

Figure 2. Experimental unit review form. Reproduced by permission of Exxon Research & Engineering Co.

EXPECTATIONS

It is important to realize that initial reaction to any new environmental review program can be less than enthusiastic. Reactions such as "That's time consuming" can come from supervisors. "I don't know that information" and "I can't be bothered—that's not my problem" are common. That is why management support must be provided and indicated directly to all respective employees.

Interest and support increases with employee interaction and familiarity. Reviews prompt discussion on the effects of chemicals and the operation of the unit that they might want or be required to know. Reviews also increase the potential for cleaner, more environmentally acceptable processes and equipment. In some organizations this may expedite commercialization and patents, leading to company profitability, employee recognition and possible career advancements.

Once a program has been in effect, a company can also expect to see less hazardous waste being generated and discarded. In many instances, an extra 10 to 20 percent capital cost can be justifiable if it reduces hazardous waste and its rapidly escalating disposal and tracking costs.

SUMMARY

An environmental review strategy for research and development activities has been described so as to assist organizations in the creation of environmental review programs for their activities. This strategy is founded on five basic concepts which, when combined, can create a strong, purposeful environmental review program. Such a program has the potential to assist in site environmental compliance and in developing processes and equipment which are environmentally-sound as well as cost-effective. ER&E's review program has been reviewed, along with comments on realistic expectations.

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Heterogeneous Ozonation Kinetics of Pollutants in Wastewater

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Ozonation is a technically viable wastewater treatment alternative for achieving stringent effluent limitations. Limited feasibility data have been reported in the literature on a wide range of pollutants. These data are primarily time concentration profiles for semi-batch air-ozone or oxygen ozone gas phase contacting with pollutant-water systems. These data have been evaluated and correlated where possible in correlations of a form suitable for scaleup to continuous systems. Pollutants include ammonia, phenol, styrene and cyanides.

INTRODUCTION

Ozone, a molecule with an extremely high oxidation potential, is a treatment alternative for controlling effluent concentrations of aqueous phase toxics. Water contaminants which have been successfully removed with ozone include phenols, cyanides, alcohols, pesticides, aldehydes and sulfides. Although ozone has had limited applications to wastewater treatment, the economics become more attractive as regulatory restrictions for effluent toxic contaminants are tightened. Ozone is also a candidate technology for removal of pollutants in groundwater at superfund sites.

In studying the ozonation of toxic contaminants in water, it is desirable to have models which can describe the decomposition kinetics of these pollutants. Although models can be developed from theoretical considerations, the inherent complexities and uncertainty in the reaction mechanisms make the use of these models undesirable in many instances. Empirical models however, although not involved with the specifics of the reaction mechanism, provide a useful method for relating the important parameters of the reaction system to the kinetic rate.

A study of the heterogeneous reactions between gaseous ozone in oxygen or air and selected contaminants in an aqueous phase was performed. A survey of the literature dealing with such reactions was conducted and where sufficient data was presented, the overall reaction order and a global rate constant for the disappearance of the pollutants were determined. For continuous flow reactors this was done by a steady state material balance on the component being treated. For a given observed reaction order n , the global rate constant is given by:

$$K_n = \frac{Q(C_0 - C)}{VC^n} \quad (1)$$

where:

K_n = the global rate constant
 n = the apparent reaction order
 C = the outlet concentration of the contaminant

C_0 = the inlet concentration of the contaminant
 Q = the liquid volumetric flow rate
 V = the reactor volume

For a semi-batch reactor, the kinetic order was determined by using a least squares regression fit of the appropriate integrated form of the rate expression:

$$\frac{-dC}{dt} = K_n C^n \quad (2)$$

where:

C = the contaminant concentration in the reactor
 t = time

Although the aqueous ozone concentration is not included in the rate expression, as these values were not reported in the literature, good correlations were obtained in most cases. After the determination of the apparent kinetic order was made, an empirical relationship between the global rate constant, K_n , and the significant observable parameters of the system were developed when possible.

LITERATURE SURVEY

The reactions between ozone and solutes and the daughter products formed during oxidation in an aqueous phase are difficult to characterize. This heterogeneous reaction system has inherent complexities. Much of the literature on ozone reactions addresses the chemical mechanisms in an attempt to better describe the physical situation. The mechanisms associated with intrinsic aqueous ozone-pollutant reactions have been shown to depend on the pH of the solution [1, 2]. The existence of multiple intermediates has been observed in the ozone oxidation of various compounds. The intermediates may be further oxidized in the presence of ozone resulting in multiple reactions. As a result of this complex behavior many investigators have worked on postulates to explain ozonation reactions [3-15]. Another complication of ozonation reactions arises from the instability of the

ozone molecule. Hence the kinetics of ozone decomposition are of importance and have been studied in many investigations [3-5, 16-30]. Although much research has been done on ozonation reactions, the actual kinetics and reaction mechanisms are for the most part still uncertain for heterogeneous ozonation systems.

Most of the literature reviewed on ozonation reactions contained very little data which were useful in meeting the objectives of this investigation. Data required for analysis included variation in observable parameters which influence the rate of contaminant decomposition. Nineteen references contained sufficient data to determine the reaction kinetic constants applicable to the system. Of these, 9 involved phenolic wastes, 6 cyanide wastes and 1 contained both. Other wastes which were examined include ammonia, styrene, benzaldehyde, benzoic acid, methanol and furfural. A more detailed literature review on heterogeneous ozonation is given by Whitlow [31].

HETEROGENEOUS MODELING

The reaction of ozone and toxic contaminants is affected by the mass transfer of ozone into the reaction regime as well as the intrinsic kinetics of the process. As with any process involving simultaneous mass transfer and reaction, the species continuity equations can be used to describe the system. In general, however, simplifications must be made to these equations to model a process. A simplification which is commonly used to describe gas-liquid reaction systems is based on the film theory, which considers the bulk gas and liquid phases to be separated by stagnant gas and liquid films. Although numerical solutions have been obtained for a set of coupled differential equations generated by a model of this type [32], the reaction scheme must be greatly simplified. This approach is inadequate to describe the complexities encountered in ozonation reaction systems. Thus it is desirable to obtain simplified approaches to describe such systems.

The method we used was a modification of that used by Kingsley [33] to model the reaction between liquid lauryl alcohol and gaseous HCl. This type of model combines all of the mass transfer interactions and reactions which take place in the system, in terms of a global rate constant. Unlike theoretical models which must account for the diffusion and intrinsic kinetics in the reaction system, this model is concerned only with the effect of observable parameters on the overall kinetic rate. Parameters which are known to affect the global rate constant and are readily observable for the ozone reaction system include pH, ozone application rate and initial concentration of the liquid phase contaminant. Hence an equation can be written in the form:

$$K_n = \alpha(G/V)^x([OH^-])^y(C_0)^z \quad (3)$$

where:

G/V = ozone application rate

$[OH^-]$ = the hydroxyl ion concentration

C_0 = the initial concentration of the water contaminant

α, x, y, z = empirically determined constants

The constants given in equation 3 are determined by a multiple linear regression between the global rate constant and the given parameters.

RESULTS AND DISCUSSION

The experimental conditions for the studies investigated [3, 8, 34-51] are summarized in Table 1. A wide range of conditions can be observed, although for some of the investigations the initial concentration and pH were not varied. Thus for these cases it was not possible to obtain an empirical relationship in terms of the parameter held constant.

For phenol ozonation, the best fit of the literature data was obtained with first order kinetics. Table 2 gives a summary of the results obtained from the regression analysis of the investigations of phenol ozonation. The study

TABLE 1. SUMMARY OF EXPERIMENTAL CONDITIONS FOR THE OZONATION OF CONTAMINANTS IN THE INVESTIGATED STUDIES

Investigator	G/V (mol/l min)	C ₀ (ppm)	pH	Volume (liters)	pH Buffer	Temp. (°C)
PHENOLS						
Moench	2.6-16.0E-4	50-500	2-12	2.0-2.5	Yes	23
Li	6.9-27.8E-5	45	2-12	6.0	Yes	25
Eisenhauer	3.0-32.8E-5	50-300	5.57	1.0	No	23
Guroi	1.5-10.4E-4	47-376	3-8.9	.565	No	20
Gould	7.6-35.8E-4	10-104	2-11	.50	Yes	23
Ward	9.0-143E-8	80-170	11.5-12.8	222-934	No	N.R.
Kroop	6.3-11.5E-4	2700	8.1-11.2	.40	No	N.R.
Hirota	2.1-3.9E-4	139	2.5-10.5	4.32	Yes	27
Anderson	1.2-2.2E-4	955-1050	7.4-11.4	1.3	No	N.R.
CYANIDES						
Garrison	4.6-403E-5	7-41000	10.5-13.0	5.85	No	25
Sondak	4.5-46.5E-5	40.5-814	10.0-12.4	2.3	Some	30-80
Zeevalkink	4.9-30.3E-5	78-94	11.8	5.7	Yes	20
Bollyky	7.2-61.3E-5	1.2-78	7-12.9	2250	No	14-20
Novak	3.4-66.7E-5	35.4	9.5	.5	No	22
Selm	2.1-2.5E-4	44.5-82.5	7.4-8.8	10.3	No	28-30
Kemker ^a	7.9-32.5E-5	29.3-387	2-11.5	2.0	No	23-25
OTHER COMPOUNDS						
McGrane ^b	1.3-20.3E-4	157-2275	2.6-12	2.75	Yes	22-50
Yocum ^c	3.1-4.3E-4	95-329	2-11	20	No	15-25
Singer ^d	6.3-26.9E-4	10-50	7-9	3.05	Yes	20

^a Phenol and Thiocyanate

^b Methanol and Furfural

^c Styrene, Benzoic Acid and Benzaldehyde

^d Ammonia

TABLE 2. COMPARISON OF THE REGRESSION RESULTS FOR PHENOL OZONATION WITH FIRST ORDER KINETICS

Investigator	α	x	y	z	I.D.	#Pts.	$\bar{I}.D.^a$
Moench	1.105	.712	-.666	.0288	.936	18	.993
Moench ^b	.434	1.01	-1.19	.0303	.944	61	—
Li	1249	.933	—	.0440	.957	9	.975
Eisenhauer	.119	.822	-.960	—	.984	13	.991
Gurol	2.38	1.02	-.809	—	.960	8	.964
Gould	.593	.724	-.783	.0685	.832	26	—
Ward	93.7	.537	-.0021	-.134	1.0	7	.929
Kroop	2.55	.392	—	.160	.969	3	.969
Hirota		No Correlation Obtained				7	—
Anderson ^b		No Correlation Obtained				9	—

$$K_1 = a(G/V)^x([PhOH])^y([OH^-])^z$$

^a Average Indices of Determination for the Time versus Concentration data

^b CSTR

performed by Moench [34] had similar objectives to this investigation and a wide range in the observable parameters was intentionally introduced into the work. Figure 1 gives a comparison of the experimental data of Moench to the models generated from his work. Figures 2 and 3 give comparisons of the models generated from the analysis of the data obtained by several investigators. These models, although generated from different experimental conditions, show relatively good agreement for the predicted rate constants. No comparisons were made for the CSTR data since only two investigators reported steady state data of this type for which a correlation was obtained [34, 43].

Much of the work on cyanide ozonation has been done with plating wastes. In this investigation, zero order kinetics was determined to give the best fit of the data examined on cyanide ozonation. Table 3 gives a summary of the model parameters determined for cyanide ozonation. A comparison of the models generated from the re-

gression analysis for plating wastes is given in Figure 4. As with phenol, good agreement is observed among these models.

A study done by Kemker *et al.* [49] included ozonation with both phenol and thiocyanate in the water. Correlations were not obtained for the decomposition of either contaminant using the initial concentration of the single species as a regression variable. When both species were included in the regression analysis however, a high index of determination was obtained. The rate expressions were simplified when the initial concentrations of both contaminants were replaced by the initial mole fraction of the species of interest. The resulting regression equations were:

Phenol:

$$K_0 = .080(G/V)^{.754}([OH^-])^{-.0263}(X_{PhOH})^{1.02} \quad (4)$$

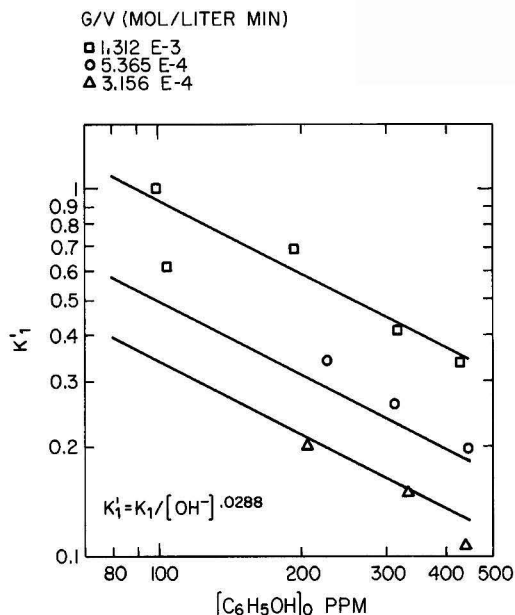


Figure 1. Comparison of the first order rate constants predicted from the regression model, to those determined from Moench's semi-batch data for selected runs.

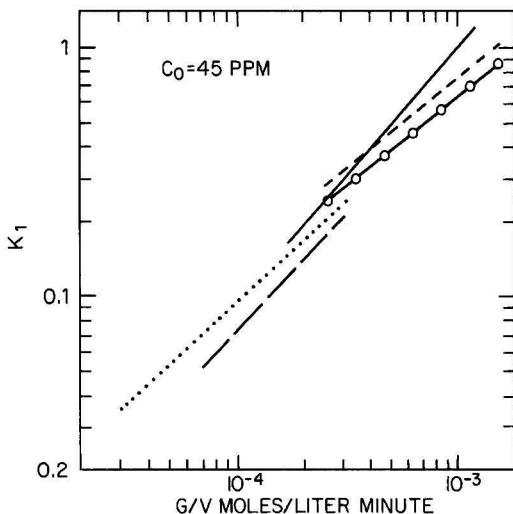


Figure 2. Comparison of the regression models for the semi-batch ozonation of phenol using first order kinetics at constant pH and initial concentration.

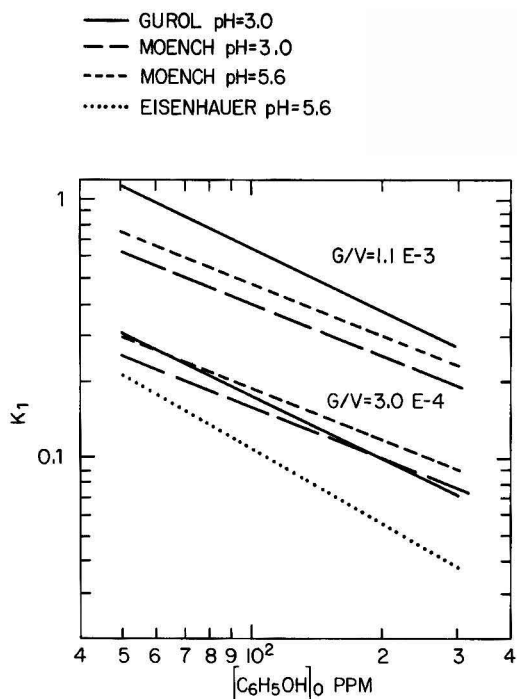


Figure 3. Comparison of the regression models for the semi-batch ozonation of phenol using first order kinetics at constant pH and ozone application rate.

Thiocyanate:

$$K_0 = .298(G/V)^{.911}([OH])^{-.0237}(X_{SCN})^{1.00} \quad (5)$$

where:

$X_{\Phi OH_0}$ = the initial mole fraction of phenol
 X_{SCN_0} = the initial mole fraction of thiocyanate

A summary of the results from other ozonation systems studied are given in Table 4. Correlations could only be obtained for the work done by McGrane on methanol and furfural. The studies for which a correlation could not be obtained were observed to have little variability in the

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 — GARRISON
 - - - ZEEVALKINK

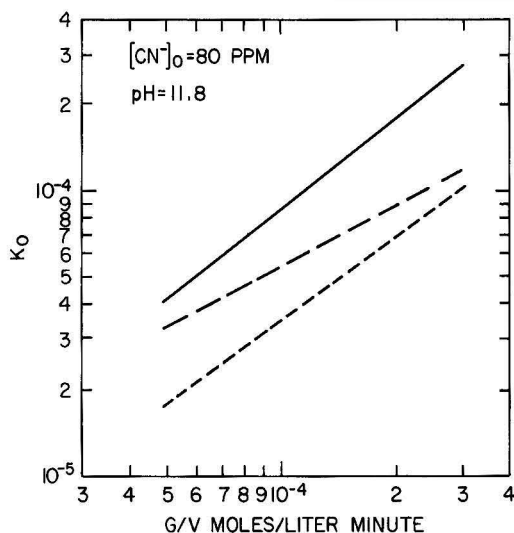


Figure 4. Comparison of the regression models for the ozonation of cyanide using zero order kinetics at constant pH and initial concentration.

parameters of interest and hence may have resulted in the failure to obtain rate expressions. The lack of variability in the observable parameters is also attributed to the studies on phenol and cyanide which could not be correlated.

CONCLUSIONS

The parameters which have the greatest influence on the kinetics of the ozonation reaction system were pH, initial contaminant concentration and ozone application

TABLE 3. COMPARISON OF THE REGRESSION RESULTS FOR CYANIDE OZONATION WITH ZERO ORDER KINETICS

Investigator	α	x	y	z	w	I.D.	#Pts.	Conditions
Garrison	1.00	1.06	-.0876	.0201	—	.979	11	All points used
Garrison	.730	.994	-.0303	.0327	—	.997	8	Syn. wastes omitted
Sondak	.579	.825	-.194	.223	—	.940	37	Temp = 30°C
Sondak	.217	.868	-.016	-.052	—	.945	28	Temp = 50°C
Sondak	5.99	.883	.496	.0356	—	.980	12	Temp = 80°C
Sondak	.343	.864	-.087	.0502	—	.933	77	Temp = 30-80°C
Sondak	1.23	.866	-.137	.120	292	.936	77	Temp included
Sondak	.212	.706	0	.0567	177	.921	24	Plating solutions
Sondak	.013	.780	-.109	.0474	-720	.910	13	pH buffered
Sondak	.159	.829	-.006	.001	-.054	.907	125	All points included
Zeevalkink	1.79E6	.963	2.73	—	—	.834	17	—
Bollyky	.0153	.0742	.975	.0006	—	.997	32	CSTR
Novak			No Correlation Obtained				3	—
Selm			No Correlation Obtained				37	CSTR

$K_0 = \alpha(G/V)^x([\Phi OH])^y([OH^-])^z \exp(w/T)$
 T = temperature in degrees Kelvin

TABLE 4. SUMMARY OF REGRESSION RESULTS FOR CONTAMINANTS OTHER THAN PHENOLS AND CYANIDES USING FIRST ORDER KINETICS

Investigator	Compound	α	x	y	z	I.D.	#Pts.	I.D. ^a
McGrane	Methanol	.748	1.02	-.885	.0043	.95	27	.983
McGrane	Methanol ^b	1.95	1.00	-.879	.164	.88	15	—
McGrane	Furfural	.214	.923	-.824	-.0718	.97	24	.957
McGrane	Furfural ^b	2.29	1.31	-1.36	-.0581	.97	17	—
Yocum	Styrene			No Correlation Obtained			10	.960
Yocum	Benzaldehyde			No Correlation Obtained			10	.973
Yocum	Benzoic Acid			No Correlation Obtained			10	.982
Singer	Ammonia			No Correlation Obtained			13	.987

$$K_1 = \alpha(G/V)^n([\Phi OH]_0)^n/([OH^-])^n$$

^a Average Indices of Determination for the Time versus Concentration Data

^b CSTR

rate. The models developed lump mass transfer intrusions from the diffusional resistance of ozone and the complex reaction kinetics, to describe the global rate. The strong influence of the ozone application rate and the initial contaminant concentration on the global rate for the systems studied, indicates that mass transfer is significant. Surprisingly good agreement was obtained between the various investigators. It should be recognized that the different investigators used different spargers and mixing arrangements, hence the mass transfer coefficients would not be expected to be identical.

The results of the analysis performed on the ozonation studies given in the literature indicates the merit and versatility of this type of empirical model. The results of this study give a method for which scale-up of wastewater ozonation equipment can be obtained from bench-scale experiments. Care should be exercised however, to avoid improper conclusions. In using a model derived from semi-batch bench scale data to scale up a continuous reaction system, the possibility of a shift in the controlling regime should be recognized. To avoid this error, it is recommended that scale up be done from data on a bench reactor which is similar to the system being designed. Hence, continuous bench scale data should be taken for use in designing a continuous ozonation system and likewise semi-batch data should be taken for the design of a semi-batch system. Caution should be exercised if the models generated are extrapolated outside the range of conditions used in the investigation. In addition, if volatile contaminants are present in the wastewater, the affect of air stripping could be significant and hence should be accounted for in the design. Air stripping was neglected by the investigators cited in this analysis.

NOTATION

a, b, c	reaction orders
C	concentration of contaminant (mol/l)
G	ozone application rate (mol/min)
G/V	ozone application rate (mol/l-min)
K_n	global rate constant of order n
n	apparent reaction order
$[OH^-]$	hydroxyl ion concentration (mol/l)
Q	liquid volumetric flowrate (l/min)
t	time (sec)
T	temperature (°K)
V	reaction volume (l)
X	mole fraction of contaminant
α, x, y, w, z	regression constants
ΦOH	phenol

Subscripts

0	initial
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Nanofiltration Extends the Range of Membrane Filtration

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Nanofiltration is a pressure driven membrane process between reverse osmosis and ultrafiltration. The rejection is low for salts with monovalent anion and nonionized organics with molecular weight below 150 while high for salts with di- and multivalent anions and organics with molecular weight above 300. Examples of applications are removal of color and TOC from Florida surface water, removal of hardness, radium, and sulfate from well water, removal of sulfate from seawater and simultaneous removal of sodium chloride and concentration of organics with molecular weight 300-1000 in the food and pharmaceutical industries. The investment cost for a nanofiltration plant is about the same as for a brackish water reverse osmosis plant, but the energy savings can be considerable by using nanofiltration instead of reverse osmosis.

INTRODUCTION

There are no completely accepted definitions of reverse osmosis (RO) (also called hyperfiltration) and ultrafiltration (UF). One suggested definition is that if the solvent flow through the membrane is by convective flow through pores, it is ultrafiltration; if it is by diffusive flow through the polymer matrix, it is reverse osmosis. However, there is no good way to determine how much of the solvent flow through a tight membrane is by "pore flow". Other suggested definitions are based on the membrane's molecular weight (MW) cutoff. MW cutoff 500 means that molecules with MW above 500 are rejected and those below 500 not rejected by the membrane. Typically membranes with MW cutoff 1000 and above are considered UF membranes and those with MW cutoff below 500 are RO membranes. However, no membrane has a sharp cutoff value, so still there must be a grey area between RO and UF.

In the 1970's, Israel Desalination Engineering coined the word Hybrid Filtration for a process between RO and UF; rejection of sodium chloride was in the range of 50 to 70 percent, while that of organics in the 90 percent range. The main disadvantage with the name Hybrid Filtration is that it does not in itself describe what type of filtration it is. It might as well be something between a media filtration and cartridge filtration. A process intermediate between RO and UF rejects molecules which have a size in the order of one nanometer. Then a suitable name for it is nanofiltration.

NANOFILTRATION MEMBRANES

Presently FilmTec has four commercial nanofiltration membranes, NF50, NF70, NF40 and NF40HF. NF stands

for nanofiltration. NF50 and NF70 are crosslinked aromatic polyamides with the same basic structure as the FT30 membrane. NF40 and NF40HF are also crosslinked polyamides with proprietary compositions. All four have a negative surface charge, which, has not been quantified. Some of their operating conditions and performances are shown in Table 1.

For all the NF membranes, rejection of magnesium sulfate is fairly high (90-98 percent), while the rejection of sodium chloride is in the 50 percent range or lower. Since the NF membranes are negatively charged, it is the anion repulsion which mainly determines the solute rejection. For example the rejection of calcium chloride is about the same (can even be lower), than that of sodium chloride while rejection of sodium sulfate is about the same as that for magnesium sulfate. Di- and multivalent anions are

TABLE 1. OPERATING CONDITIONS AND PERFORMANCE FOR FILMTEC NF MEMBRANES

	NF50	NF70	NF40	NF40HF
Pressure to produce 43 l/m ² /h permeate flux*, bar	4	6	20	9
Operating pH range	2-10	3-9	2-10	5-8
Max. Temp., °C	45	45	45	45
Approximate solute Rejection**				
NaCl	50	70	45	40
MgSO ₄	90	98	95	95
Glucose (MW 180)	90	98	90	90
Sucrose (MW 342)	98	99	98	98

* At 25°C and 0.2% MgSO₄

** At 25°C, 0.2% solute conc. and about 43 l/m²/h permeate flux

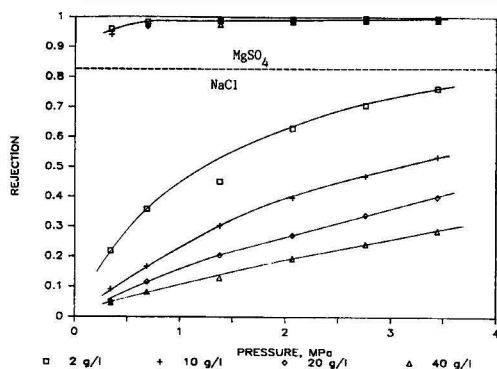


Figure 1. Rejection of magnesium sulfate and sodium chloride for a NF40-2514 element at 20°C. Rejection is based on average salt concentration at membrane/brine interface.

highly rejected. So far, no known case has evolved where highly charged cations have interacted with the NF membranes to give a positive net surface charge.

As shown in Table 1, NF50 and NF70 operates at low pressures with low TDS waters, about the same pressure as for ultrafiltration, while NF40 operates at about the same pressure as low pressure reverse osmosis. NF40HF is somewhere between. There is one important performance difference between NF40 and NF40HF on one hand and NF50 and NF70 on the other hand, and that is how rejection of sodium chloride is affected by sodium chloride concentration. At constant permeate flux, sodium chloride rejection is about constant for NF50 and NF70 even with increasing sodium chloride concentration. For NF40 and NF40HF, sodium chloride rejection decreases with increasing sodium chloride concentration. This can be explained by the Donnan exclusion model. The higher the concentration of sodium chloride, the more sodium ions are available to shield the negative charges on the membrane making it easier for the chloride ions to pass the membrane. The sulfate ion has a higher charge den-

sity than the chloride ion and is almost completely repelled by the NF membrane even in as high ionic strength solution as seawater or 4 percent magnesium sulfate.

Figure 1 is taken from Eriksson (1986) and shows measured rejection of magnesium sulfate and sodium chloride for a NF40-2514 element. At 20 bar pressure, sodium chloride rejection drops from 60 percent to 20 percent when sodium chloride concentration increases from 2 g/l to 40 g/l. A minor part of this loss in rejection is a function of the 35 percent decrease in permeate flux, but the major part is due to a five-fold increase in the salt permeability through the membrane. This element had a magnesium sulfate rejection above 99 percent.

NANOFILTRATION APPLICATIONS

Nanofiltration applications can be arranged in mainly two groups:

Partial Water desalination: Here the objective is to decrease the TDS generally of the water, or to specifically decrease the concentration of one or a few species while the remaining ones do not matter. Especially when a big percentage of the anions is sulfate, a high salt rejection is obtained. In these cases nanofiltration has to compete with reverse osmosis. The advantage with nanofiltration is the lower operating pressure, resulting in lower energy costs and possible investment savings in pump and piping. If the objective is only a reduction of overall TDS, it might sometimes be less expensive to treat part of the water with reverse osmosis and blend RO permeate with raw water to produce required amount of product water. Then reverse osmosis could result in savings through a smaller plant compared to nanofiltration. However, if the objective is to primarily remove one or more species which are highly rejected with NF membranes, reverse osmosis does not have this advantage.

Separation of salts with monovalent anions from organics in the MW range 300-1000: These separations cannot be carried out with reverse osmosis or ultrafiltration. Competing processes are electrodialysis (ED) and ion exchange (IX). Nanofiltration has an advantage over ED and

TABLE 2. MEMBRANE PERFORMANCE FOR SURFACE WATER AT OLGA, FLORIDA (Taylor 1985)

	Pres. bar	Temp. °C	Perm. Rec%	TOC mg/l	Color cpu	Alk. ppm as CaCO ₃	T. Hardness ppm as CaCO ₃	CL mg/l	TDS mg/l	pH
Raw Water				16-22	70	110-127	200-220	63-90	334-484	7.5-7.9
				Rejection* %						
NF50	4.5	22	50	94	96	76	77	52	84	7.6
UF**	6.9	28	71	56	82	7	14	3	17	7.5

* Rejection is based on feed concentrations

** Desal V90-G10 MW cutoff 2000 membrane

TABLE 3. NF70 PERFORMANCE FOR WELL WATER NEAR DES MOINES, IOWA

	Feed mg/l	Rej.* %		Feed mg/l	Rej.* %		Feed mg/l	Rej.* %		Feed mg/l	Rej. %
Na ⁺	119	64	Ca ²⁺	58	88	Cl	30	45	Iron	0.32	100
K ⁺	9.0	64	Mg ²⁺	23	88	Alk.**	246	59	Silicon	3.8	28
			Str ²⁺	2.1	90	F ⁻	1.7	29	Phosphorus	0.7	60
			Ba ²⁺	0.01	100	SO ₄ ²⁻	204	98	Boron	1.2	4

* Based on average of feed and concentrate

** Alkalinity as ppm as CaCO₃

IX in its ability to simultaneously concentrate the higher MW compound in the same separation step. NF40 and NF40HF membranes are predominately used for these applications because of their very low rejection of sodium chloride at high salt concentration.

Some specific nanofiltration applications are described below.

Organics Removal from Surface Water

Seven different membranes, (5 UF, 1 NF, and 1 RO) all in spiral wound element form, were tested at Olga, Florida. The results from the NF (NF50), and the tightest tested UF membrane are shown in Table 2.

The NF50 membrane is operating at a lower pressure than the UF membrane and has about 95 percent rejection of TOC and color, much higher than for the UF membrane. As expected the UF membrane has very low rejection of inorganic ions, while the NF50 membrane gave about 77 percent rejection of hardness and alkalinity and about 50 percent rejection of chloride. The NF50 membrane was heavily fouled during this test so permeate flux decreased to 17 l/m²/h.

Well Water Desalination

Four NF70-4040 elements in series were tested on well water near Des Moines, Iowa. Feed, permeate and concentrate were analyzed. Both the mass balances for individual ions or elements and charge balance were very close, indicating accurate analysis. The result is shown in Table 3.

Rejection of sulfate is very high, and about 98 percent, while rejection of monovalent anions is in the 30-60 percent range. Rejection of bicarbonate (alkalinity) is higher than that for chloride. This is also the case for the NF50 membrane, which Table 2 shows. The rejection of silicon and boron are low, 28 percent and 4 percent respectively. The relatively high percentage of sulfate in the feed results in a high rejection of cations, especially divalent cations (hardness), which show about 90 percent rejection. The high rejection of hardness makes the NF70 membrane suitable for water softening, replacing lime softening. This is discussed by Hickman *et al.* (1985) and Conlon (1985).

Radium Removal

In several places in the U.S.A., the groundwater contains radium at higher concentration than considered safe. Many communities in Wisconsin and northern Illi-

nois have this problem, which they must solve within a few years. Three processes are presently considered for removal of radium, ion exchange softening, lime softening, and nanofiltration. One advantage with nanofiltration is that there is no problem with disposal of radioactive contaminated solids materials, in possible contrast to the sludge in lime softening or the spent resin in ion exchange softening. The radium concentration in the nanofiltration concentrate at practical permeate recoveries (75-85 percent) is low enough for easy disposal. Probably we will know in two years which process or processes are most suitable for radium removal.

Sulfate Removal from Seawater

Oil yield from an oil well is increased by pumping down water which forces up oil. In places like the North Sea there is barium present in the oil well, which causes barium sulfate to precipitate when in contact with the sulfate in the seawater. The precipitate will block the channels through which the water must flow to displace oil. Reverse osmosis has been considered to remove the sulfate from seawater. However, nanofiltration can do this to a considerably lower cost because of lower pressure and higher permeate recovery system. The NF40 membrane is the most suitable here because of its very low rejection of sodium chloride at high salt concentrations, which is shown in Table 4. Required pressure is only about 13 bar at 20°C. However, it is not known yet whether 96 percent rejection of sulfate is enough to prevent barium sulfate precipitation in the oil well.

Nanofiltration/Ion Exchange for Nitrate Removal

In many agricultural areas the concentration of nitrate in the groundwater is above recommended levels for drinking water. Reverse osmosis can be used to remove most of the nitrate together with the other solutes, but discharge of the concentrate presents a problem in inland areas. One demonstration plant in West Germany successfully uses evaporation of the RO concentrate. However, removal of nitrates by ion exchange is more common in West Germany. The ion exchange resin preferably takes up di- or multivalent anions, e.g., sulfate, so when these are present in significant amounts, the resin has to be regenerated frequently. The time between regeneration can be typically increased two to three times by feeding the ion exchange unit with permeate from a NF membrane. Then the ion exchange effluent is combined with the NF concentrate according to Figure 2.

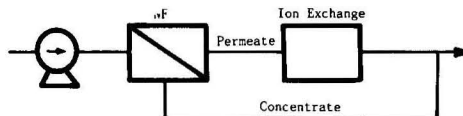


Figure 2. Combined nanofiltration and ion exchange to remove nitrate.

TABLE 4. NANOFILTRATION TO REMOVE SULFATE FROM SEAWATER

Feed: Synthetic seawater, 20°C (sodium, calcium, magnesium, chlorine and sulfate according to ASTM specifications)
Operating conditions: Batchwise concentration at a varying pressure to maintain a constant permeate flux of 34 l/m²/h until 75 percent permeate recovery had been obtained.

	Pressure, bar		Cumulative Permeate Conductivity	Sulfate Rejection*
	Start	End	Feed Conductivity	
NF40	11	13	.93	96
NF50	18	25	.74	95
NF70	28	39	.47	97

* Based on cumulative permeate and feed concentrations.

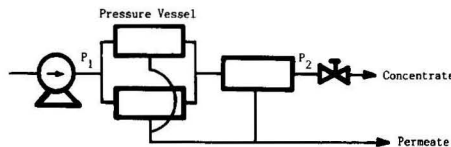


Figure 3. Typical RO unit design.

Tests in West Germany achieved essentially zero nitrate rejection and above 90 percent sulfate rejection for a NF membrane. A patent has been applied for this process.

FOOD AND PHARMACEUTICAL INDUSTRIES

The Food and pharmaceutical industries generate many liquids containing both sodium chloride and organics with molecular weight 300-1000, where it is desired to concentrate the organics and remove the sodium chloride. The NF40 and NF40HF membranes are the most suitable for these applications because of their low sodium chloride rejection. However, little can be presented about these applications because of the cloak and secrecy placed over them by these industries.

One application which can be mentioned here is the treatment of a salty cheese whey in the dairy industry. The volume of this salt whey is small compared to normal cheese whey, but it creates a major waste disposal problem. It contains about four to six percent sodium chloride, and if this is mixed with the normal cheese whey, the mixture becomes too salty to be suitable as, e.g., cattle feed. It has a high BOD, mainly from lactose and proteins, and adding this to an existing small waste water treatment plant would cause overloading. The NF40 membrane separates the salt whey into a permeate stream (75% of feed) which has a BOD low enough to go to the waste water plant, and a four-fold concentrate stream (25% of feed) which contains less than two percent sodium chloride and can be mixed with the normal cheese whey. The sodium chloride concentration in the NF40 concentrate is reduced to levels below the incoming whey by diafiltration.

SYSTEM DESIGN WITH NANOFILTRATION SPIRAL WOUND ELEMENTS

For water desalination a typical reverse osmosis unit looks like Figure 3. When spiral wound elements are

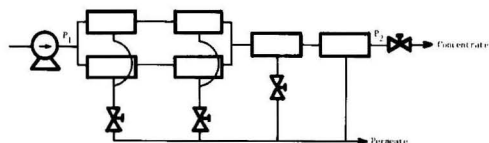


Figure 4. Unit with permeate backpressure.

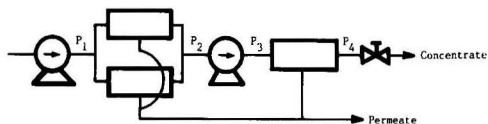


Figure 5. Unit with booster pump.

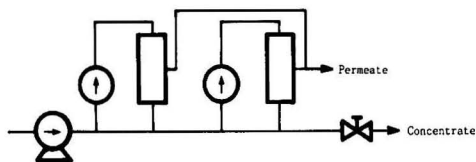


Figure 6. Unit with recirculation.

used, each pressure vessel contains up to six one-meter long elements with a typical pressure drop ($P_1 - P_2$) over the unit of about 4 bar. This design would not be optimum for water desalination using NF50 or NF70 membrane. A difference of 4 bar pressure for these membranes would either give a very low permeate flux for the downstream elements or too high a flux for the upstream elements. A high permeate flux causes rapid fouling of the membrane, which can be difficult to reverse through cleaning and causes poor membrane performance. A nanofiltration membrane is as easily fouled as a reverse osmosis one. This means that to produce a given amount of permeate flow, just as much membrane area must be used for nanofiltration as is used for reverse osmosis. Thus, for the most practical applications there is no reduction in the required number of elements when changing from RO to NF membrane. There are generally three ways to overcome the problem of too much pressure drop over the unit: permeate backpressure, interstage booster pump, and recirculation. These are illustrated in Figures 4-6.

Permeate backpressure is applied by a valve or orifice in the permeate line from the upstream pressure vessels. Then the feed pressure can be raised without causing too high a flux for the upstream elements and still get high enough pressure for the downstream elements. Such a system is now operating in Iowa. It is a mobile plant and consists of six pressure vessels arranged in a 2-2-1-1 array, as in Figure 4, each with three NF70-8040 elements, totaling 18 elements. At one site, permeate back pressure was 2.1 bar, 1.4 bar, and 0.7 bar in the three first arrays respectively. Feed was 23 m³/h, 18°C, 10 bar with 208 microsiemens/cm conductivity. Permeate flow rate was 17 m³/h and conductivity rejection 75 percent based on feed data. Rejection data for the same plant operating at Wayland, Iowa are shown on Table 5. Flow data are not known at this site.

Another way to increase the pressure for the downstream elements is to install a booster pump as illustrated in Figure 5. This is more energy efficient than using permeate backpressure, but adds extra complexity and one more moving part subject to failure. For large systems, a booster pump will probably be more attractive than permeate backpressure because of energy savings.

Recirculation systems are used frequently today for ultrafiltration, which is a low pressure operation. Figure 6 shows two stages, but there might be only one, three or even more stages. Recirculation systems are more flexible but more expensive than single pass systems shown in Figure 4 and 5. In applications where the processed liquid causes substantially rapid membrane fouling, e.g., in most food applications, recirculation plants will be predominating for nanofiltration as they are today for ultrafiltration and reverse osmosis.

TABLE 5. NF70 MEMBRANE PERFORMANCE FOR WELL WATER AT WAYLAND, IOWA

18 NF70-8040 Elements

Permeate recovery: about 82% (from ion analyses)

	Feed mg/L	Rejection* %		Feed mg/L	Rejection* %
Na ⁺	190	79	Cl ⁻	71	63
K ⁺	20	81	NO ₃ ⁻	7	34
Ca ⁺⁺	100	96	SO ₄ ⁺⁺	580	96
Mg ⁺⁺	46	96	Cond.**	1600	85

* Based on feed concentration

** Conductivity in microsiemens/cm

Economy

No direct cost data for nanofiltration will be presented here but only a rough comparison with the cost for the same size reverse osmosis plant. The main costs for a reverse osmosis or nanofiltration plant are capital, membrane replacement, labor, and energy consumption. The investment cost and thus, also the capital cost for a nanofiltration plant is about the same as for a brackish water reverse osmosis plant with the same capacity. This is because: 1) some savings can be made in using lower pressure pumps and piping; 2) cost is the same for pretreatment and instrumentation; 3) the same amount of membrane area is needed, but nanofiltration elements are generally somewhat more expensive than reverse osmosis elements.

The membrane replacement cost is slightly higher for a nanofiltration plant than for corresponding reverse osmosis plant because of the higher element cost. The labor cost is the same. The big difference is in energy cost, where the savings with nanofiltration can be large because of the much lower operating pressure. In summary the investment cost for a nanofiltration plant is about the same as the same size brackish water reverse osmosis desalination plant, but big savings in energy cost can be made.

CONCLUSION

Nanofiltration with charged membranes opens new areas for membrane filtration, separation between mono-

valent anion salts on one hand and di- and multivalent anion salts and organics with MW above 300 on the other hand. Nanofiltration is also a low energy alternative to reverse osmosis where only partial water desalination is required. Big potential markets are liquid separations in the food and pharmaceutical industries, and water and wastewater treatment.

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Low NO_x, High Efficiency Multistaged Burner: Gaseous Fuel Results

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A multistaged combustion burner design is being evaluated on a 0.6 MW package boiler simulator for in-furnace NO_x control and high combustion efficiency. A low NO_x precombustion chamber burner has been reduced in size by approximately a factor of two (from a 600 ms first-stage residence time to 250 ms), and, for additional NO_x control, coupled with [1] air staging, resulting in a three-stage configuration, and [2] natural gas fuel staging, yielding up to four stoichiometric zones. Natural gas, doped with ammonia to yield a 5.8 percent fuel nitrogen content, was used to simulate a high nitrogen content fuel/waste mixture. In low NO_x burner baseline tests, without advanced staging, a 315 ppm NO emission (measured dry, corrected to zero percent O₂) was measured, compared with an emission of 1000 ppm measured using a conventional, unstaged burner. Both of the multistaged combustion modifications for additional NO_x control reduced NO emissions by an additional 50 percent, to 160 ppm meeting the program goal. However, air staging application resulted in the entire front end of the boiler being fuel-rich, whereas fuel staging, or reburning, in the boiler required only a small fuel-rich flame core in the boiler. Further, no boiler penetrations were necessary with reburning modification, as staged fuel and air were injected through the boiler front wall; access for burnout air injection deep into the boiler was necessary for the air staging modification. Thus, the four-stage configuration, combining the precombustion chamber burner and reburning, appears to be the most promising approach for minimizing NO emissions and maximizing primary fuel/waste destruction.

INTRODUCTION

The family of nitrogen oxide compounds, including nitric oxide (NO) and nitrogen dioxide (NO₂), is generally referred to as "NO_x." These NO_x are formed during the combustion of coal, oil, and natural gas by the reduction and oxidation of molecular nitrogen (N₂) and nitrogen contained in the fuel. NO₂ is a poisonous gas that the United States Environmental Protection Agency (EPA) has designated as a criteria pollutant because of its human health effects [1, 2]. Further, NO_x are known to contribute to the formation of photochemical oxidants and are pre-

cursors, along with sulfur oxides (SO_x), of acid precipitation. Two more areas of concern are emerging in regard to NO_x levels in the atmosphere. First, forest damage, reported to be extensive in the Federal Republic of Germany [3], has been linked with increasing NO_x levels. Second, increasing levels of atmospheric nitrous oxide (N₂O) have been measured, levels that have been predicted to contribute to both a decline in the abundance of stratospheric ozone and an increase in climatic warming

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[4]. Studies of N_2O and NO concentrations in experimental flames and in flue gases have shown that a strong correlation exists between these two gases formed in combustion processes.

The EPA estimates that about 20 million tons (18,000 Gg) of NO_x are emitted annually from stationary and mobility sources in the United States. Unlike SO_x emissions, NO_x emissions have been increasing [5]. Coal- and oil-fired utility and industrial boilers account for over half of the NO_x emissions. Only 15 percent of these stationary sources are regulated by EPA's New Source Performance Standards (NSPS) [6]; the remainder must be addressed with retrofit technologies if significant NO_x emission reduction is to be realized. Another NO_x control problem is posed by the potential of incinerating high nitrogen content wastes in industrial boilers. While incineration of these materials would not constitute a significant increase in the overall national NO_x emission level, individual plant emissions may be sufficient to result in a local NO_x problem and, thus, prevent on-site incineration from being permitted. With thermal destruction being an attractive alternative to landfill storage of wastes, there continues to be a need for developing high efficiency, low NO_x combustion technologies.

By far, the major portion of NO_x has been found to be NO. Much is known about the mechanisms of NO formation in flames, both from molecular nitrogen (source of thermal NO) and from fuel-bound nitrogen (source of fuel NO). Thermal NO can be reduced by decreasing peak flame temperatures. Fuel NO, not as strongly dependent on temperature, is very sensitive to reactant stoichiometry. Fuel-rich conditions promote N_2 formation over NO formation. Laboratory studies and field test data have established the importance of fuel NO to the total emission of NO_x from residual fuel oil and coal flames. Therefore, minimizing NO_x formation in flames typically involves controlling air and fuel mixing rates to create fuel-rich reducing zones and extracting heat to reduce final oxidation temperatures.

To avoid the need for costly post-combustion NO_x removal, several in-furnace NO_x control strategies have been developed and applied to boilers. These include reduced air preheat, load reduction, low excess air, flue gas recirculation, overfire air, deep air staging, fuel staging (or reburning), and various low- NO_x burner systems [7], while NO_x emissions can be reduced by 20 to 80 percent using these technologies, from uncontrolled levels exceeding 1000 ppm for some high nitrogen content coals, application of these combustion modifications can result in reductions in combustion efficiency and increases in sooting and slagging in the boiler. This problem is of particular concern in the boiler co-firing of fuels and wastes, where high waste destruction efficiencies and minimal formation of other incomplete combustion products are of paramount importance. The purpose of this work is to investigate various multistaged combustion concepts for burning high nitrogen fuel/waste streams with low NO_x emissions and high combustion efficiency. Specifically, tests were designed to evaluate the use of a precombustion chamber burner, modified to reduce burner size, coupled with air or air/fuel staging. A NO_x emission of less than 0.2 lb (as NO_2)/10⁶ Btu* (or approximately 175 ppm NO_x **) for firing gaseous and liquid fuels doped with up to 5 percent nitrogen (by weight) was targeted. In this paper pilot-scale test results with gaseous fuel firing are presented; results with fuel oil/pyridine firing are being published separately.

* The current NSPS for large industrial boilers firing high nitrogen heavy fuel oil is 0.4 lb/10⁶ Btu. This standard is under review. (1 lb/10⁶ Btu = 0.43 kg/GJ.)

** All NO_x /NO emissions reported in this paper are referenced to a dry measurement corrected to zero percent O_2 .

Before describing the experimental procedure and results, some background information is provided.

Precombustion Chamber Burner

The precombustion chamber burner is a staged combustion technology capable of achieving a NO_x emission of less than 0.1 lb (as NO_2)/10⁶ Btu (or approximately 90 ppm NO_x), even with high nitrogen fuel firing [8]. It consists of a primary air and fuel injection system, a large refractory wall precombustion chamber, and a secondary air injection section. Fuel and primary air are injected with rapid mixing into the nearly adiabatic precombustion chamber with a first-stage stoichiometry of between 0.6 and 0.8.*** A residence time between 0.6 and 1.0 s allows for maximum reduction and conversion of fuel nitrogen species to N_2 in the fuel-rich precombustion chamber. First-stage combustion gas products exit the burner through a convergent section which minimizes both radiative heat loss to the boiler and back-mixing of the secondary air. The transition section between the burner and boiler is water-cooled to reduce combustion gas temperatures before final air addition. The precombustion chamber burner has been tested on a full-scale (16 MW) crude oil-fired steam generator used for thermally enhanced oil recovery (TEOR) in Kern County, CA [9]. A 30-day continuous monitoring test demonstrated the burner's ability to maintain a nominal NO_x emission of 70 ppm with a high combustion efficiency [10]. During burner optimization testing, NO_x , CO, and smoke emissions were measured over a range of first-stage stoichiometries. These data indicate the sensitivity of NO_x emission to first-stage stoichiometry and the good hydrocarbon burnout characteristics of the burner. Earlier pilot-scale tests firing nitrogen-free fuels suggest that the minimum NO_x level of about 50 ppm can be attributed to second-stage thermal NO_x formation.

A test designed to demonstrate the potential for using this burner for nitrogenous waste incineration was performed at EPA's Air and Energy Engineering Research Laboratory. A pilot-scale (0.6 MW) precombustion chamber burner was used to incinerate a surrogate nitrogenous waste mixture of 9.1 percent (by volume) pyridine in fuel oil. A NO_x emission of less than 100 ppm was maintained, with greater than six nines (99.9999 percent) destruction of the pyridine being achieved. The relative NO_x emissions with and without pyridine addition indicate that less than 1 percent of the fuel nitrogen was converted to NO_x . This preliminary result sparked interest in utilizing the precombustion chamber burner for high efficiency, low NO_x combustion.

However, while the precombustion chamber burner has been demonstrated successfully in pilot-scale and field tests, its large size makes it impractical for most boiler retrofit applications. Reducing the burner size results in insufficient first-stage residence time to fully convert the fuel nitrogen to N_2 ; hence, higher NO_x emissions result. Additional NO_x control can be achieved by further staging of the combustion process in the boiler.

Staged Combustion

The concept of staged combustion consists of injecting secondary air into the boiler downstream of the primary combustion zone, which is characterized by substoichiometric levels of combustion air. This concept may be employed by utilizing overfire air ports, secondary air injectors, or burners-out-of-service. In applications with a

*** The stoichiometric ratio (SR), the actual air-to-fuel ratio divided by the theoretical air-to-fuel ratio, is used throughout this paper.

shortened precombustion chamber burner, further air staging would extend the fuel-rich first stage from the burner into the boiler.

Reburning

As many as 30 years ago, experimental results were available indicating that NO_x could be destroyed by reaction with hydrocarbon radicals. Early fundamental studies of NO_x destruction by injection of secondary fuel into the flame zone were performed by Wendt *et al.* [11] who coined the name "reburning" to describe the process. Concerted effort to develop reburning for application to boilers occurred in Japan during the late 1970's and early 1980's. The first reporting of these efforts was by Takahashi *et al.*, [12] documenting extensive laboratory-, pilot-, and full-scale evaluations of a fuel staging process they refer to as Mitsubishi Advanced Control Technology, or MACT.

Since 1982 EPA has carried out both in-house and extramural bench- and pilot-scale reburning tests. In-house experiments have focussed on natural gas and fuel oil reburning [13-16]. Significant findings include defining the dependence of reburn effectiveness on primary flame NO_x level, reburn zone stoichiometry, and reburn fuel nitrogen content. Fifty percent NO_x reduction is possible with 10 to 20 percent of the fuel used for reburning. At low primary NO_x levels, however, a nitrogen-free reburning fuel (such as natural gas) must be used to achieve 50 percent reduction. Tests have shown that reburning is effective over a wide range of temperatures and with relatively short reburning zone residence times (0.2 to 0.4 s).

In application with a shortened precombustion chamber burner, reburning would result in a four-stage combustion process. Because much of the primary fuel has been reduced prior to boiler entry, reburning might be applied from the front wall of the boiler. Such reburning application would simplify the boiler retrofit requirements by not requiring multiple boiler penetrations.

EXPERIMENTAL PROCEDURE

The goal of this study is to minimize NO_x formation, with an emission target of 175 ppm or less, and maintain efficient incineration in the combustion of surrogate fuel/waste mixtures with up to 5 percent fuel nitrogen by using a precombustion chamber burner reduced in size by about half.

The unmodified facility, shown schematically in Figure 1a, is comprised of a precombustion chamber burner and a package boiler simulator. The precombustion chamber burner consists of a primary fuel and air injection module, two 0.89 m long spool modules with 0.51 m internal diameter, and a 0.33 m long convergent module. These burner modules have a thick refractory wall lining to minimize heat loss, maintaining the high temperatures that promote conversion of fuel nitrogen to N₂ under fuel-rich stoichiometries. To achieve rapid mixing in the precombustion chamber, the primary fuel is injected through a divergent nozzle and the primary air, which is not preheated, is passed through fixed swirl vanes. The convergent module minimizes back-mixing of combustion gas and radiation loss to the boiler. A water-cooled transition module, 0.25 m in internal diameter, cools the combustion gas before secondary air addition to minimize thermal NO_x generation. Primary fuel nitrogen is simulated by doping ammonia into natural gas or pyridine into distillate fuel oil. All of the results reported here are with the gaseous fuel.

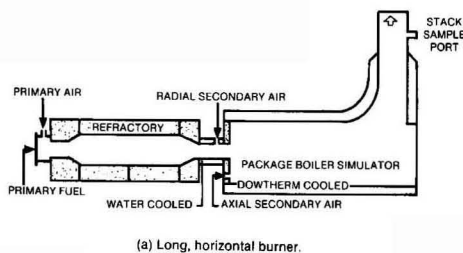
The pilot-scale boiler simulator is rated at 0.9 MW thermal input. The boiler's radiant section is horizontal, 0.6 m in diameter, 3.0 m long, and cooled with Dowtherm C® heat transfer fluid. Combustion gas exits the boiler through a vertical stack. The boiler's front face has eight axial ports for addition of staged air.

The research facility was modified as shown in Figure 1b. The horizontal 2.62 m long precombustion chamber burner was replaced with a shorter 1.80 m long vertical burner. This shorter burner, with a nominal residence time of 250 ms, has all the essential design features of the long horizontal burner, which has a nominal residence time of 600 ms. The elbow section has a 5 cm diameter port for staging fuel into the burner. Two of the eight axial air ports on the boiler front face were modified to provide ports for staging fuel into the boiler at an angle of 45 degrees. This design allows for reburning application from the boiler front face, the aerodynamic separation of the fuel-lean and fuel-rich zones in the boiler. The end plate of the boiler has been modified to allow the insertion of a water-cooled boom for deep staging of air into the boiler.

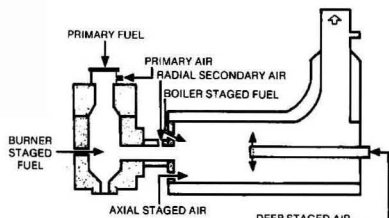
The experimental facility is designed for independent control and measurement of each fuel, fuel dopant, and air stream. Stack gas speciation is measured by a continuous emissions monitoring system. NO and NO_x are measured by chemiluminescence. Spot-check measurement of NO_x indicated that NO emissions accounted for over 95 percent of the exhaust NO_x emissions. In this paper only NO measurements are reported.

A North American Scotch-type package boiler (N.A.) was used to provide conventional burner results to be compared with the multistaged burner results. This boiler is a three-pass unit with a continuous service rating of 0.3 kg of steam per second (2400 lb/hr). Its size and thermal characteristics are nearly identical to those of the package boiler simulator [9, 10].

Evaluated were burner baseline performance and burner operation with various air staging and fuel staging NO_x controls. The parameters affecting the NO_x emissions from the facility without additional NO_x controls are fuel nitrogen content, combustion gas residence time in the precombustion chamber, first-stage stoichiometry, and exhaust stoichiometry. The residence time of combustion



(a) Long, horizontal burner.



(b) Short, vertical burner.

Figure 1. Pilot-scale combustion research facility. The package boiler simulator has been fitted with a precombustion chamber burner and air and fuel staging ports.

gas in the burner depends on precombustion chamber length, load, and stoichiometry. The nominal load was 0.6 MW. The exhaust stoichiometry was kept at a nominal value of 15 percent excess air, as per commercial boiler practice. Nominal fuel nitrogen content was 5.8 percent (by weight), as ammonia doped in natural gas.

BURNER BASELINE CHARACTERIZATION

During burner baseline characterization tests, the effects of burner length, first-stage stoichiometry, excess air, load, and fuel nitrogen content on NO emissions were studied. Three burner configurations, two with a horizontal orientation and residence times of 600 and 350 ms and one with a vertical orientation and a residence time of 250 ms, were evaluated, and compared to data using a conventional, unstaged burner.

Burner Stoichiometry Variation

First-stage stoichiometry was varied by changing the primary and secondary air inputs while maintaining an overall 15 percent excess air. The results of these tests are plotted in Figure 2. Two curves (square and triangle symbols) in the figure correspond to the long (two spool modules) and short (one spool module) configurations of the unmodified facility (Figure 1a). The third curve (circle symbols) corresponds to the facility configuration used in

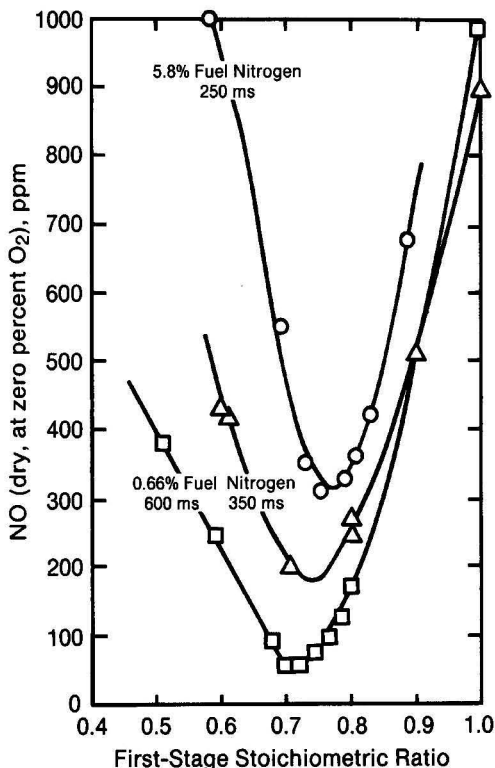


Figure 2. Effect of burner size and fuel nitrogen content. The square and triangle symbols correspond to test data with the long and short (respectively) horizontal burner firing natural gas containing 0.66 percent nitrogen as ammonia. The circle symbols represent data with the vertical burner firing natural gas containing 5.8 percent nitrogen as ammonia.

the rest of this study (Figure 1b). The curves indicate a strong sensitivity of stack NO to changes in first-stage stoichiometry. For the long, horizontal burner configuration, with a residence time of 600 ms, the minimum stack NO concentration was 60 ppm at a primary fuel nitrogen content of 0.66 percent. With the short, horizontal burner configuration, with a residence time of 350 ms, the minimum NO stack concentration rose to 200 ppm at the same fuel nitrogen content. In the vertical burner, when firing a fuel with 5.8 percent fuel nitrogen, a minimum NO emission of 315 ppm at a first-stage stoichiometry of 0.78 was achieved. Thus, additional combustion modifications are necessary to achieve the program goal of 175 ppm maximum NO emission with the new burner configuration.

Excess Air Variation

The effect of excess air variation on stack NO is shown in Figure 3. Excess air had a much stronger effect in the unstaged North American burner tests than in the low NO_x burner tests, as expected. While reducing excess air did provide some NO reduction, maintaining an exhaust excess air level of 15 percent is important for achieving high combustion efficiency.

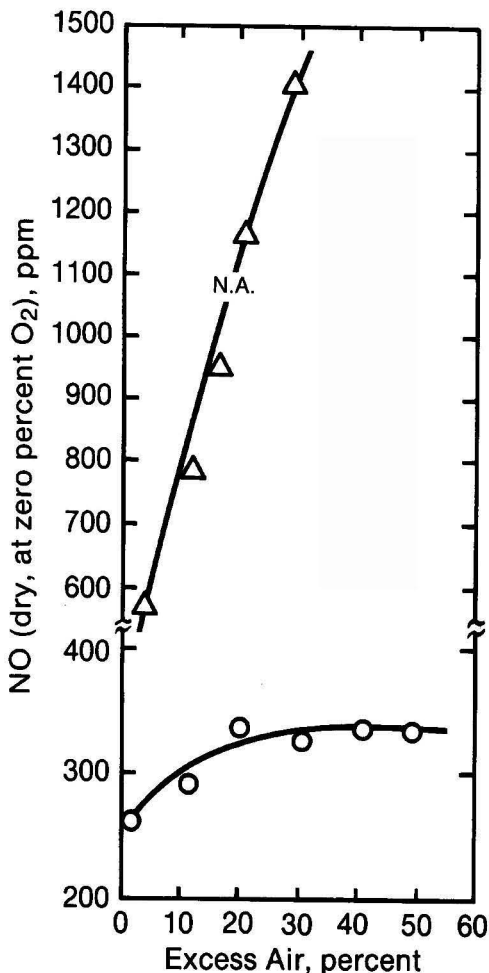


Figure 3. Excess air variation results for the unstaged North American burner and the low NO_x burner.

Load Variation

The effect of load reduction on stack NO is shown in Figure 4. With the unstaged burner, NO emissions were reduced only slightly with burner derating, due to decreased air-fuel mixing intensity. However, with the low NO_x burner, the effect was much greater because load reduction corresponds to an increase in first-stage residence time and, thus, a decrease in NO emission. As load was decreased from a nominal condition of 0.6 MW to about 65 percent of nominal, the stack NO concentration dropped from 315 to 260 ppm in the low NO_x burner tests. Reducing load by 35 percent increased the residence time from 250 ms to about 385 ms. However, boiler steam requirements may make load reduction an impractical means of NO_x control.

Fuel Nitrogen Variation

The effect of fuel nitrogen variation, which is analogous to varying the amount of nitrogenous waste (ammonia-doped natural gas with 6 percent nitrogen) co-fired with a nitrogen-free fuel (natural gas), is shown in Figure 5. Data are plotted for the full range of co-firing conditions, from 100 percent fuel to 100 percent surrogate waste. Exhaust NO level increased with increasing fuel nitrogen content in the fuel/waste stream, as expected, with a much greater sensitivity observed in the conventional North American burner tests. These results demonstrate the precombustion chamber burner's ability to reduce fuel nitrogen to molecular nitrogen, even with its reduced size (250 ms). The full size (600 to 800 ms) precombustion chamber burner produces NO emissions even less sensitive to fuel nitrogen content [8].

AIR STAGED NO_x CONTROLS

During air staged NO_x control tests, the effect of moving the location of secondary air addition, from the radial ports in the transition section to the axial and deep staged ports in the boiler, was examined. The secondary air was distributed between radial and axial locations in one series of staging tests and between radial and deep staged ports (located 132 cm from the boiler front face) in a second series of tests. A water-cooled boom, aligned with the

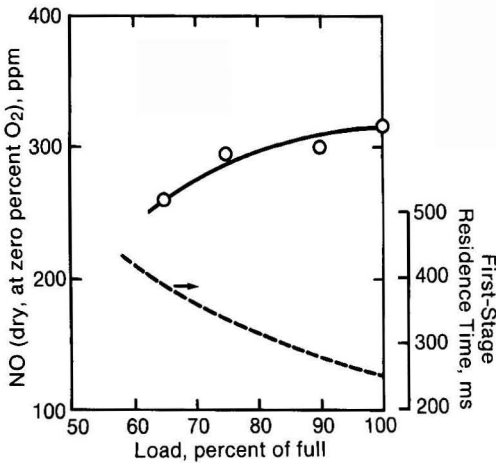


Figure 4. Load variation results for the low NO_x burner.

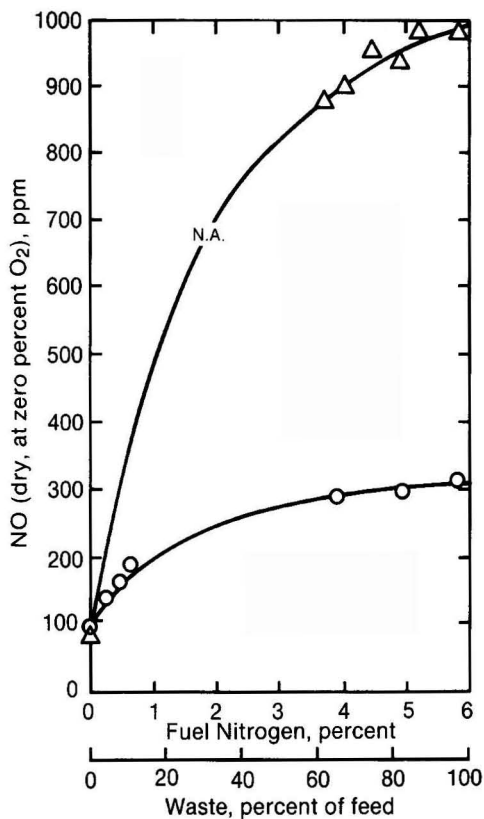


Figure 5. Fuel/waste nitrogen variation results for the unstaged North American burner and the low NO_x burner.

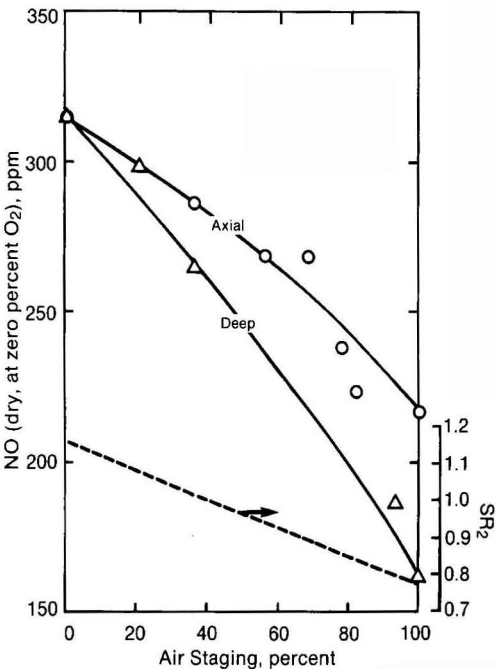


Figure 6. Air staging results.

centerline of the boiler, was used to supply the deep staged air. First-stage stoichiometry was optimized for each test condition.

Test results for the two cases of secondary air staging in the boiler are shown in Figure 6. The axial air staging results show a drop in minimum NO concentration from 315 ppm with no staging to 220 ppm with 100 percent of the secondary combustion air moved from the radial injectors to the axial injectors. The temperature of the combustion gases is higher in the transition section than in the boiler; also, the mixing of secondary air and combustion gas is more rapid when the secondary air is added radially into the transition section. Hence, more thermal NO is generated and more fuel nitrogen species fragments are oxidized with radial air addition into the transition section than with axial addition into the boiler. Similarly, lower temperatures in the boiler at the deep staged air location and longer fuel-rich zone residence time result in a lower NO emission when the secondary air is deep staged. With all of the secondary air being added from the deep staged location, the minimum NO level was 160 ppm.

Based on the test results just described, the deep staging of secondary air is an effective means of minimizing NO emissions. However, such staging may lead to burn-out problems, which is of great concern when co-firing waste. Extending the fuel-rich zone from the precombustion chamber into the boiler exposes the reducing combustion gases to the cool boiler walls, which may result in slagging and/or sooting. Further, the lower combustion gas temperatures in the boiler slow the fuel-rich nitrogen kinetics.

FUEL STAGED NO_x CONTROLS

During fuel staged NO_x control tests, the effect of diverting part of the primary fuel to staged locations in the burner and boiler was studied. The stage fuel was natural gas, with no ammonia dopant. The first-stage stoichiometry was optimized with respect to NO emission. In the case of fuel staging in the burner, the secondary natural gas was added, using a water-cooled boom, down the centerline of the boiler; secondary air was added axially into the boiler to allow sufficient fuel-rich zone residence time. In the case of fuel staging in the boiler, the secondary natural gas was added at an angle of 45 degrees, using two water-cooled booms, from ports in the boiler front face. Secondary air to complete primary fuel combustion was added radially into the transition section, while burn-out air for secondary fuel combustion was added axially into the boiler, using six axial ports on the boiler front face.

Burner Fuel Staging Results

Holding total load constant, fuel was diverted from the primary fuel injector to a secondary injector near the precombustion chamber exit (see Figure 1b), thus creating two stoichiometric zones in the burner in addition to the burnout zone in the boiler. The staged fuel, undoped natural gas, provides a burst of hydrocarbon radicals that accelerate the reduction of primary fuel nitrogen to N₂ prior to secondary air injection. Secondary air was injected through the axial injectors. The results, plotted in Figure 7, show a decrease in NO emission with increasing fuel staging. Two effects contribute to this decrease in NO emissions with fuel staging: (1) fuel nitrogen reduction mechanisms are accelerated due to increased radical concentrations, and (2) combustion gases from the high nitrogen content primary fuel are diluted by the combustion gases from the nitrogen-free secondary fuel. With 35 percent of the fuel staged, the exhaust NO levels decreased

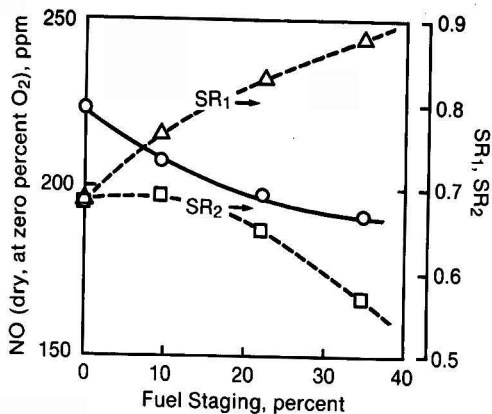


Figure 7. Burner fuel staging results.

to 190 ppm, from 220 ppm at zero percent staging (and axial secondary air addition). The figure also shows that the optimum first-stage burner stoichiometry (SR₁) increases with increasing fuel staging, while the optimum second-stage burner stoichiometry (SR₂) decreases slightly. This result is consistent with kinetic model predictions of optimum stoichiometries for the two burner stages. A first-stage stoichiometry of 90 percent theoretical air should result in a higher destruction efficiency of the primary fuel/waste stream than with a more fuel-rich first stage.

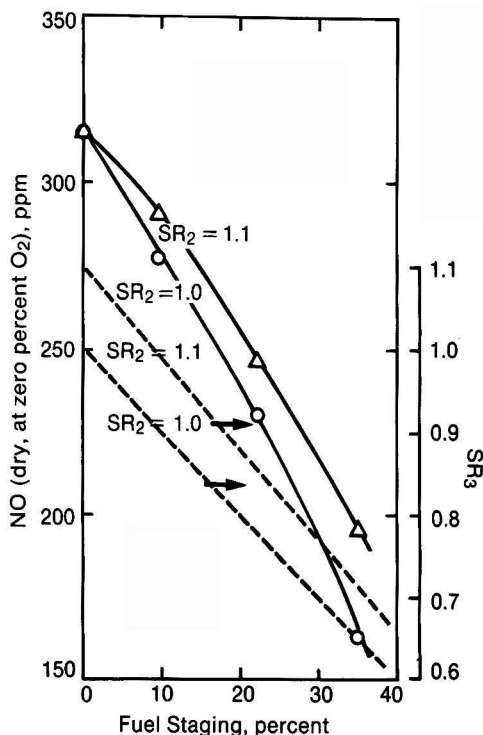


Figure 8. Boiler fuel staging results.

As in the tests just described, total boiler load was held constant while fuel was diverted from the primary fuel injector to a secondary injector. In this case, the staged fuel (undoped natural gas) was injected into the boiler downstream of the secondary radial air addition. Thus, a four-stage combustion process is established, consisting of a fuel-rich burner zone and three boiler zones characteristic of reburning (i.e., fuel-lean, fuel-rich, fuel-lean). As already described, all of the staged air and fuel flows were injected from the front face of the boiler at various angles, resulting in the three boiler stoichiometric zones. Figure 8 shows that the NO emissions decrease with an increase in fuel staging. This is due to both primary NO destruction and primary combustion gas dilution. Two second-stage stoichiometries (SR_2) were established: 1.1 and 1.0. With 35 percent fuel staging, the exhaust NO levels were reduced to 195 ppm (from 315 ppm) at a SR_2 of 1.1, and to 160 ppm at a SR_2 of 1.0. Due to less distinct stoichiometric zones than typically established in reburning application and incomplete nitrogen chemistry in the primary flame, the NO reduction by fuel staging is not quite as great as that obtained when the staged fuel is injected farther downstream of the fuel-lean primary combustion zone [12]. However, the configuration used in these tests required no boiler penetrations. With this multistaged combustion, the NO_x emission goal of 175 ppm was met. In addition, the complete destruction of the primary fuel/waste stream appears to be ensured by providing all of the required primary combustion air prior to entry into the boiler, and then passing the primary combustion gases through a secondary flame.

DISCUSSION AND CONCLUSIONS

Results from the various combustion modification schemes for the reduction of NO are summarized in Table I. These results were obtained at optimal first-stage stoichiometries. From the table it can be seen that deep air staging and fuel staging in the boiler are most effective in minimizing NO emissions, with an overall conversion of fuel nitrogen to molecular nitrogen of 98 percent. However, deep air staging not only presents problems of hardware modification due to boiler penetrations, but may also lead to incomplete combustion. On the other hand, the boiler fuel staging hardware modifications used in this study were designed with retrofit feasibility and efficient combustion in mind. In the tests described here, all of the secondary combustion air necessary for primary fuel burnout is introduced with rapid mixing at high temperatures in the water-cooled transition section between the burner and boiler. Further, the staged fuel and air from the front face of the boiler provide a secondary flame for increased primary fuel/waste destruction, similar to incinerator afterburners.

Some mention must be made of the limitations of these results. First, little information has been collected to date on surrogate fuel/waste burnout. Burning natural gas and ammonia mixtures, rather than the liquid and solid fuel/waste mixtures that are encountered in practice, allows for well-controlled parametric testing for NO_x emission evaluation, but it does not provide for good burnout simulation. Stack emissions of CO were less than 10 ppm for every test condition reported here. However, in-furnace sampling provides insight into the potential for fuel burnout problems. Another problem involved in testing with natural gas is the simplified mixing processes and faster kinetics characteristic of gaseous fuel combustion. First-stage fuel nitrogen conversion to molecular nitrogen is expected to be lower for less volatile fuels.

Configuration	Amount	Stack NO ppm (percent reduction)
Baseline		
—Unstaged Burner (N.A.)	—	1000
—Long Low NO _x Burner	600 ms	90 (91)
—Short Low NO _x Burner	250 ms	315 (68)
Low NO _x Burner Characterization		
—Excess Air	5%	290 (71)
—Load	65%	260 (74)
—Fuel Nitrogen	2%	250 (75)
Secondary Air Staging		
—Axial	100%	220 (78)
—Deep	100%	160 (84)
Fuel Staging		
—Burner	35%	190 (81)
—Boiler		
— $SR_2 = 1.1$	35%	195 (80)
— $SR_2 = 1.0$	35%	160 (84)

Another limitation of this study is that the results are applicable only in the range of temperatures characteristic of the firetube package boiler. Temperatures in the package boiler simulator range from 1700 K at the boiler entry to 1250 K at the boiler exit. To avoid high thermal NO formation in the primary combustion gas burnout, sufficient heat must be extracted in the transition section to lower the combustion gas temperatures to less than 1800 K.

Finally, note that the low NO emissions from the fuel staging tests are achieved largely by the dilution of the primary combustion gases with secondary flame gases, which do not have a fuel nitrogen input. Actual molar destruction of NO is small in these tests. However, this dilution is coupled with the NO formation and destruction processes and should not be discounted. From the standpoint of NO minimization and fuel/waste destruction maximization, the overall emissions per unit mass of input should be considered. From this perspective, fuel staging in combination with the shortened precombustion chamber burner appears to be the most attractive combustion modification for high nitrogen content fuel/waste firing in boilers.

Further characterization of this multistaged burner design is ongoing at EPA. Fuel burnout is being measured to optimize both combustion efficiency and NO emission. Fuel oil/pyridine test results will be published shortly [17].

ACKNOWLEDGMENT

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An Evaluation of Fine Particle Wet Scrubbers

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A study was undertaken to reduce emissions from a calciner stack. Tests were conducted to characterize the particle size distribution, effluent loading, and chemical composition. Several methods for reducing emissions were evaluated. The source of the effluent was found to be due to some combination of: excessive mist carryover from a spraytower, flashing of high solids concentration quench liquid, poor flow patterns, a large quantity of fine particles, condensation of metal vapors, or gas phase reaction which formed fine particles. A series of studies were conducted to improve the operation of the spray tower. As only limited success was achieved with these methods several other control devices were evaluated. This article discusses (1) the methodology used to evaluate the cause of the effluent problem, (2) the principles followed in obtaining a representative slipstream, and (3) the performance of the three devices tested, along with parameters which affect performance.

INTRODUCTION

Fine particles, especially in moisture saturated gas streams, are very difficult to capture and remove. The conventional approach for removing fine particles is to employ venturi scrubbers. Several new concepts have been suggested and have been studied by various investigators under laboratory conditions. In the real world, these devices do not always perform as well because the particles are different in size, distribution, or have physical properties, which are not the same as the particles in the laboratory tests.

When industry is faced with a significant reduction in emissions, laboratory studies are seldom sufficient to sell the technology to management. Within Monsanto, the business and manufacturing groups expect non-income producing equipment to operate at the lowest cost, from day one. To insure this, the program outlined in this paper has been used to minimize risk and cost. The example for this paper is based upon a phosphorus plant where a 95% reduction in emissions was found to be necessary on a calciner kiln.

In the phosphorus manufacturing process, various grades of ore are blended and roasted to remove soil humus, light inorganic elements, and to produce a fused phosphate rich nodule. The nodule makes downstream melting and reduction of the phosphate more efficient. In the phosphorus furnace, coke and the phosphate react to produce the elemental phosphorous and carbon monoxide. The CO gas is then used as a principal fuel source to calcine the ore in the kiln.

Emissions from the kiln are scrubbed with alkaline water to remove acid gases and particulates in a spray tower. The existing spray tower was known to be in ex-

cess of 99.9% efficient. However, large particles (>100 micron) account for most of this high performance. EPA Method 5 sampling doesn't help define the nature of an emissions problem since fine particles (<1 micron), are as likely to deposit in the probe as are particles greater than 1 micron.

PARTICLE SIZING

Two principal methods were used to define the particle size distribution (SASS train and cascade impactors). The

TABLE 1. SASS SAMPLING TRAIN RESULTS

Sample No.	Particle Size micron	Percent of Total
1	>10	2
	3-10	<1
	1-3	16
	<1	83
2	>10	5
	3-10	2
	1-3	12
	<1	80
3	>10	1
	3-10	<1
	1-3	3
	<1	95
average	>10	3
	3-10	1
	1-3	10
	<1	86

SASS sampling train gives particle cuts at 1, 3, and 10 micron and shows that most of the problem is in particles below 1 micron (Table 1). Two types of cascade impactors were used to further define the particle distribution below 1 micron. The University of Washington Pilat Mark III impactor was found to provide the most useful information for this study and became the particle sizing method for the rest of this study. Results of particle sizing with the Nelson and Pilat cascade impactors are shown in Figure 1. The smaller Nelson unit appears to overemphasize the coarse particle count, even when corrected for particle density. However, the three modes of particle formation are shown with the Nelson unit in Figure 2. Clearly the particles below 1 micron would be difficult to capture, even for a venturi scrubber. The particles in the nucleation mode do not represent much of the mass and are probably associated with P_2O_5 and other reaction species, as discussed later.

IDENTIFICATION OF CAUSE

Five possible causes of the fine particle emission problem were noted as follows:

1. Substantial quantities of metallic species are volatilized in the hot kiln and condensed as metal oxides prior to the spray tower. This type of condensation is expected to produce submicron particles.

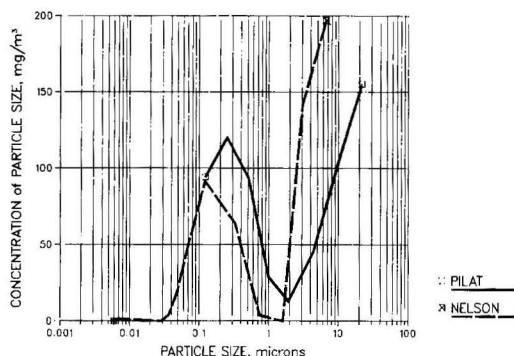


Figure 1. Cascade impactor particle sizing.

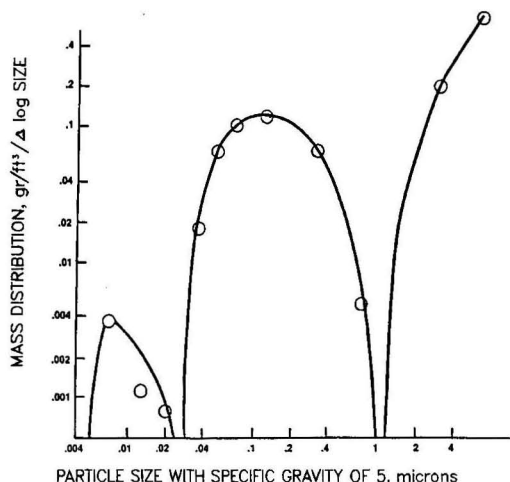


Figure 2. Differential particle size distribution—multiply gr/ft³ by 2290 to obtain mg/m³.

TABLE 2. SUMMARY OF ELEMENTAL ANALYSIS, %

Element	Particulate Concentration
Aluminum	1.15
Antimony	.17
Barium	.16
Boron	.55
Cadmium	6.23
Calcium	3.23
Chromium	.07
Cobalt	.26
Copper	.21
Fluoride	5.07
Iron	1.39
Lead	.57
Magnesium	.68
Manganese	.03
Molybdenum	.06
Nickel	.20
Phosphorus	5.59
Potassium	6.85
Silicon	2.47
Silver	.02
Tin	.02
Vanadium	.23
Zinc	32.17

2. Water droplets carried over from the spray tower could contain particulate. Evaporation of the droplets in the sampling train will result in increased particulate load.
3. Spray water droplets containing dissolved solids could be evaporated completely at the scrubber inlet, producing particles which are from 1/100 to 1/1000 of the water droplet size. The resulting submicron particles are not expected to be captured in the spray tower.
4. Dust blown out of the kiln could contain a high quantity of fine particles.
5. Phosphorous, contained in the carbon monoxide gas from the furnace, could be oxidized to P_2O_5 and only partially removed by the spray tower.

Items 2, 3, and 5 were eliminated as causes of the problem by the following program:

1. Droplets were collected and analyzed for solids loading. The droplet emission rate was measured by inference from the difference between theoretical water vapor content and condensation and droplet spatter patterns. These tests showed that droplet carryover could contribute as much as 15% of the

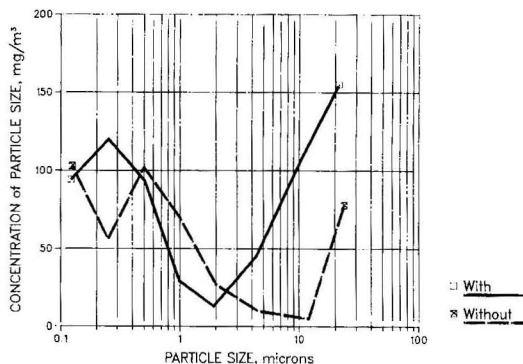


Figure 3. Particle sizing showing effect of fines recirculation.

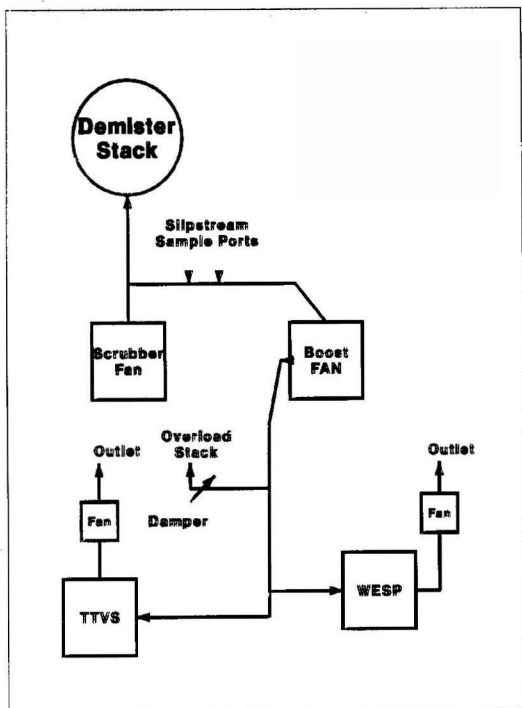


Figure 4. Diagram of slipstream ductwork.

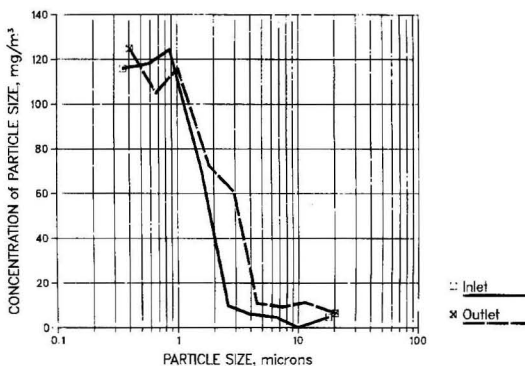


Figure 5. Slipstream particle size distribution.

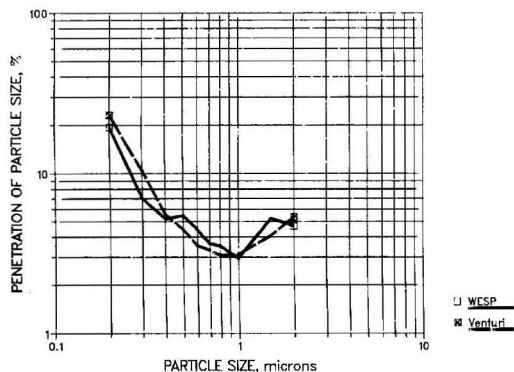


Figure 6. Scrubber performance on nodulizing kiln.

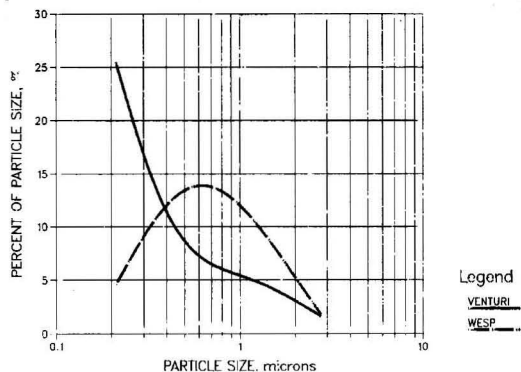


Figure 7. Scrubber exit particle size distribution.

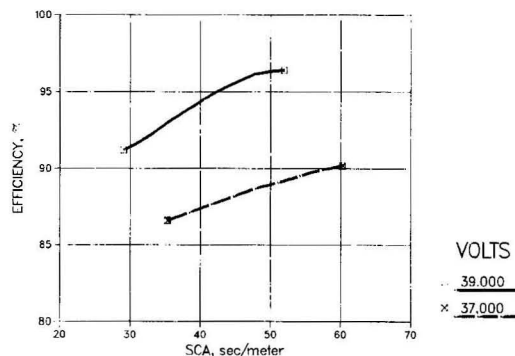


Figure 8. WESP performance vs. SCA and charging voltage.

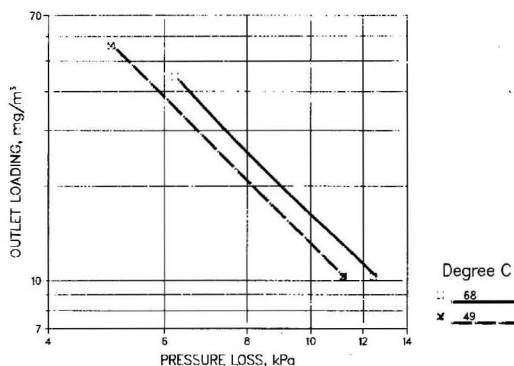


Figure 9. TTVS performance vs. pressure drop and water temperature.

emissions. However, the fine particles were not reduced by implementing steps to eliminate the carryover. A reduction of droplet carryover by 50% resulted in no reduction of emissions.

2. Fresh water was substituted for the normal recycle water used at the spray tower inlet. These tests showed little to no improvement in performance and clearly indicated that spray droplet evaporation at the inlet was not a concern.
3. The kiln was fired with coal and/or natural gas to determine the impact of P_2O_5 formation on emissions. Although during start-up of the kiln, the phos-

TABLE 3. EFFECT OF LIQUID RATE ON TTVS PERFORMANCE

Pressure Drop kilo Pascal	Water Rate kg/kg gas	Emission Rate mg/cubic meter
7.7	2.27	19
	2.31	22
	2.33	22
	2.37	22
	2.82	16
	2.91	22
	2.92	27
8.7	2.30	22
	2.34	14
	2.82	16
	2.83	27
	2.92	12
	2.97	16
9.9	2.35	21
	2.98	18
	3.00	22
	3.03	18
	3.05	21
	3.06	24
	3.15	25
	3.19	22

phorous contributes heavily to the particulate load, less than 6% of the emissions during normal operation (with ore in the kiln) were due to the CO gas.

Chemical analysis of the ore and particulate appears to support that, of the two remaining sources, the volatile inorganics which were condensing were the major source of the problem. These results are shown in Table 2 (note that over 50% of the particle would be oxides or other anions, not shown). Further analysis showed these metallic elements to be combined and not condensed metals, as would be expected to form in the spray tower.

Figure 3 shows further evidence of the effect of fine particle blowout versus the volatile metallic condensation theory. The introduction of solids previously captured by the spray tower showed an increase in emission rate but the increase was confined to particles above 2 micron. The lack of a change in the mass emission rate below 1 micron demonstrates that those particles are coming from the kiln and are not generated by comminution. A small portion of the mass of emissions may be due to volatile metals as shown by the nucleation mode particles shown in Figure 2.

SELECTION OF SUBMICRON PARTICLE COLLECTOR

It became apparent that an add-on collector would be required to meet the 95% reduction. Three devices were selected based upon reports in the literature, our experience, and cost considerations. The catenary grid scrubber (CGS) was chosen primarily because of cost and limited success with fumes. It was also selected before the extent of the fine particle problem was defined. The other two devices, wet electrostatic precipitator (WESP) and the tandem throat venturi scrubber (TTVS) were considerably more expensive, but expected to perform well. The major concerns, along with performance, were the operating cost, fouling potential, and water treatment considerations.

SLIPSTREAM DESIGN

In order to test the pilot units a representative slipstream of the emission source was needed. The source was about 30 meters above grade and the pilot units

would have to be located near grade. To insure that a representative sample of the emission is tested, a very large slipstream ($\sim 5 \text{ m}^3/\text{sec}$) was pulled from the emission source. A small slipstream ($\sim 0.5 \text{ m}^3/\text{sec}$) was then taken from the large slipstream (see Figure 4). The purpose of this type of slipstream sampling was to meet the following set of ordered objectives:

1. Maintain the particle size distribution below 1 micron
2. Retain the same particle concentration below 1 micron
3. Maintain the same PSD and particle concentration for all particle size ranges.

Because the gas was saturated with water, particle growth may occur and alter the PSD. This would result in distorted performance of the device under test. To prevent condensation and scrubbing of the particles, the ductwork was insulated and heated. Gas temperature was controlled within $2-4^\circ\text{C}$ above the pickup point. Confirming tests showed that both the PSD below 1 micron and the concentration were retained. The total particle concentration was reduced and then by only 20%. These results are shown better in Figure 5.

Approximately three months of testing were allotted for the CGS and WESP. The TTVS was tested for only a month. A good portion of the CGS test period was devoted to shakedown of the slipstream system and verifying the sampling procedures. Mechanical problems and the weather (-40°C and 31 m/sec winds) slowed things down, also. Once the PSD below 1 micron was found to be unaffected by the slipstreams, EPA method 5 testing was used to conduct routine performance tests. Confirming tests using both particle sizing and method 5 tests were used to verify the results and to provide particle specific penetration data.

SCRUBBER TEST RESULTS

The Catenary Grid Scrubber removed as much as 50% of the particles. No scaling or fouling of the grid or walls was observed. Sulfur dioxide was removed very well ($>90\%$ with caustic). Scrubbing performance was limited by water carryover at high grid velocities. The use of a fiber-pad mist eliminator to reduce mist was not successful because it plugged rapidly. In addition, the higher pressure drop due to the higher velocity was considered unacceptable ($>3000 \text{ Pa}$).

The WESP and TTVS were able to remove over 95% of the particulate. A thin film of scale on the WESP plates was easily removed with a high pressure water wash-down. The scale built up rapidly and essentially stopped, which reduced the cleaning requirements. Some scale

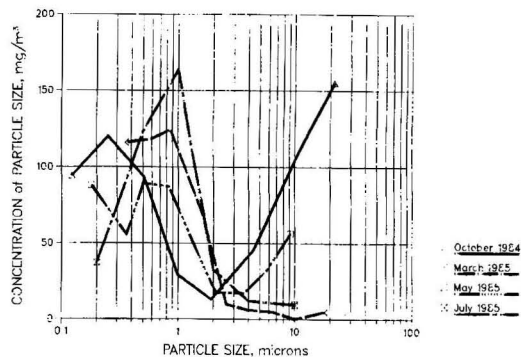


Figure 10. Particle size distribution variation.

TABLE 4. EFFECT OF PSD VARIATION ON PERFORMANCE

Particle Size microns	Conc. of Size mg/m ³	Expected Average Performance Nodulizing Kiln Scrubber			Venturi		
		WESP penet %	out mg/m ³	%	penet %	out mg/m ³	%
0.20	36.99	18.75	6.94	27.85	23.74	8.78	27.52
0.30	74.77	6.09	4.55	18.27	12.79	9.56	29.98
0.50	122.77	4.73	5.80	23.31	4.82	5.91	18.53
1.00	163.81	2.98	4.89	19.62	2.79	4.57	14.34
2.00	32.35	3.86	1.25	5.01	2.64	0.85	2.67
4.00	11.96	4.44	0.53	2.13	10.63	1.27	3.99
10.00	9.48	10.00	0.95	3.80	10.00	0.95	2.97
		inlet, mg/m ³		outlet, mg/m ³			
Total	452.12		24.90			31.90	
Particle Size microns	Conc. of Size mg/m ³	Worst Expected Performance Nodulizing Kiln Scrubber			Venturi		
		WESP penet %	out mg/m ³	%	penet %	out mg/m ³	%
0.20	121.30	18.75	22.74	47.43	23.74	28.79	44.75
0.30	115.71	6.09	7.04	14.69	12.79	14.80	23.00
0.50	90.88	4.73	4.30	8.96	4.82	4.38	6.80
1.00	35.33	2.98	1.05	2.20	2.79	0.99	1.53
2.00	20.45	3.86	0.79	1.65	2.64	0.54	0.84
4.00	45.60	4.44	2.03	4.23	10.63	4.85	7.53
10.00	100.00	10.00	10.00	20.85	10.00	10.00	15.54
		inlet, mg/m ³		outlet, mg/m ³			
Total	529.27		47.95			64.35	

also formed near the inlet of the TTVS. In both cases, the operation of the units was unrestricted and the scale was not seen as a major maintenance problem.

TTVS and WESP penetration performance is shown in Figure 6 for a set of confirming tests. The performance of the WESP is slightly better in the 0.5 to 2 micron range with a minimum at about 1.0 micron. The TTVS exhibits the classical cut-point of a venturi scrubber at about 0.5 micron. Because the fine particles represent such a large portion of the emissions, the resulting particle size distribution of the scrubber effluent amplifies the small difference in Figure 6 (see Figure 7).

Specific collection area (SCA), charging voltage, and water quality (pH, temperature, solids content) were varied during the WESP tests. The SCA and charging voltage results are summarized in Figure 8. The other parameters did not affect collection efficiency. During the initial stages of testing, plate wetting was not very uniform and performance was reduced in proportion to the estimated reduction in SCA. Adjustment of the water distribution nozzles is the most difficult and important aspects of operating a WESP. Another difficulty was plate alignment with the discharge electrodes. Since gas distribution was well controlled, the WESP performed very well once the minor difficulties were fixed. Solids in the scrubbing water, temperature changes, and low pH did not reduce performance. With a pH of about 6.5, about 50% of the sulfur oxides were removed.

For the TTVS, pressure drop, scrubbing liquid flow-rate, liquid temperature, pH, and throat configuration

were varied. Only pressure drop and water temperature changes the efficiency as shown in Figure 9. Liquid flowrate effects were not very apparent, although the ratio of water between the throats was found to have a minor effect as shown in Table 3. The ratio of pressure drop between the two throats appears to be optimized by the manufacture to match the water ratio, since configuration change caused the optimum water ratio to change. Sulfur dioxide was removed very effectively (~90%) at pH of 6.5.

CONCLUSION

Over the course of the testing program, the particle size distribution and loading were found to change due to changes in kiln operation, as shown in Figure 10. The specific penetrations found during the performance testing, and the resulting emissions would be as shown in Table 4. Clearly the WESP is less sensitive to PSD upsets. On the other hand, the TTVS performance can be improved by a slight increase in pressure drop. Since the upfront cost (capital) of a TTVS is significantly less than a WESP, the operating costs can be minimized to reduce the net annual operating cost. Final technical and cost evaluations showed the two devices are roughly equal. Because of the well defined PSD and specific penetration data, the full-scale installation is expected to control the emissions at the lowest cost.

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