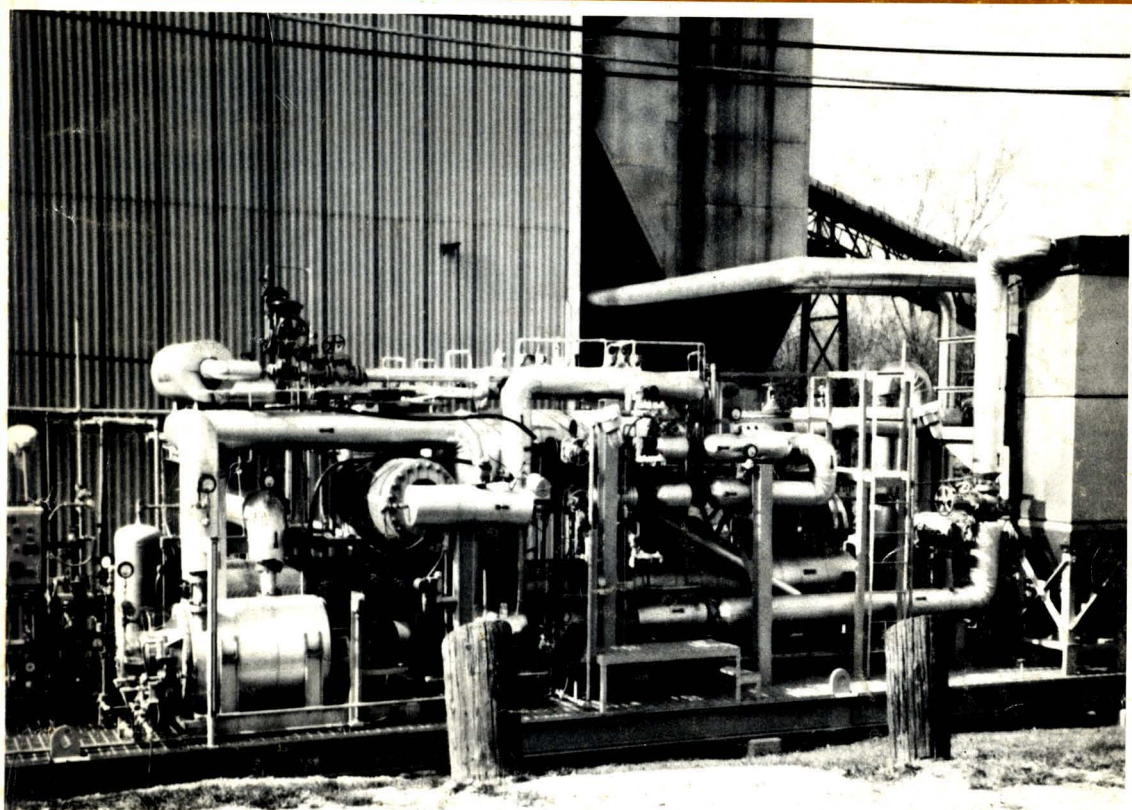# ENVIRONMENTAL PROGRESS

The Parsons Flue Gas Cleanup Pilot Plant installation at the St. Marys Municipal Power Plant, St. Marys, OH (see article on page 211). Photo courtesy of the Ralph M. Parsons Co., Pasadena, CA.

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ENVIRONMENTAL PROGRESS

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A New Climate for Solving Environmental Problems

by

Jean-Yves Perez

The liability-driven system we've used for toxic waste cleanup for the last 10 years, a litigious posture used for solving many of our problems, has proven ineffective. Problems have been resolved, but it often comes about through legal maneuvering, rather than rational technology and practical engineering.

As citizens of a world community, we need to be much more forward thinking, much more proactive and less reactive. The prevention of global pollution and toxic waste should always be our first consideration and, obviously, should precede protracted court battles. We need to replace activities that support litigation with activities that foster remediation.

Many engineers and scientists I've spoken with both here and abroad feel it's more effective to give the parties responsible for the problem—industry, for instance, incentives first, not penalties. Reducing waste streams and finding alternatives to toxins used in manufacturing are just two examples of the way industries are preventing pollution. Later, if the incentives are not taken advantage of, strict but simple enforcement is appropriate. Environmental regulations should never be so inflexible that they actually damage the industrial base.

Today's waste problems—and new waste problems in the future—lend themselves very well to incentives. Tax credits are one kind of incentive that has been used effectively in the past in other areas. Others might include the government and the responsible party cost sharing to develop a solution to clean up a problem within a given time frame. Just simplifying the regulatory process and simplifying the required documentation that goes with the process would be an incentive in itself. How to pay for cleanup and deciding who pays, remains a contentious issue. Industry leaders have often expressed to their willingness to pay their fair share, but when the requirements become excessive, they frequently object and litigate.

Despite the fact that the need is great, applying new and sometimes not well-proven technology can be risky. The present climate in the United States is not conducive to risk taking. In Europe and Australia, attempting innovative and sometimes not thoroughly tested approaches are much less difficult. This is because their regulatory process is not as established and not as rigid as those in this country.

There has been a tendency, especially with toxic contamination, to try to solve problems at the 100-percent level and not to experiment. We can solve some problems with a high rate of success, but to go beyond that level incurs tremendous costs. It may be more prudent to wait until the technology is more advanced. A health-risk based approach suggests that reducing toxic levels to below the harmful point may at times be acceptable until better technology can be found and applied. Sometimes we have found that advanced technology is not needed to protect human health as well as the environment.

Our regulations are pushing us to be perfect when perfection is not yet achievable or not financially feasible. Richard Feynman, the Nobel Prize-winning physicist, once said, "Scientific knowledge is a body of statements of varying degrees of certainty—some most unsure, some nearly unsure, but none *absolutely* certain."

We need to lift restrictions that are imposed on new technologies simply because they do not meet the letter of the law and its regulations. The intent of the laws was initially very good, but the laws haven't worked very well and have been aggravated by regulations that are too complicated to be efficient. The laws should be straightforward and more conducive to finding solutions than finding loopholes.

In the United States, we need to develop a climate that supports innovation and the introduction of new technologies, that establishes a credible technological base. All of us—society, industry, science and engineering—have learned a great deal in the last 20 years. Most importantly, we've learned that we must be better stewards of the planet.

In the next 20 years, we should consider using the carrot and not the stick approach to solving environmental problems and reducing the mistrust that currently exists. The public's trust that problems can be solved and prevented needs to be restored. The climate is right, the need is great and the technology is available from all over the world to meet the needs of man and the environment.

Jean-Yves Perez is president and chief executive officer of Woodward-Clyde, a consulting engineering firm headquartered in Denver.

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Center for Risk Management Established At ORNL

A Center for Risk Management has recently been established at the Department of Energy's Oak Ridge National Laboratory (ORNL) to focus the laboratory's resources even more strongly on evaluating risks to human health and to assist in determining priorities and solving environmental problems related to energy production and consumption.

Established with the support of the Environmental Restoration Program of Martin Marietta Energy Systems, Inc., which manages ORNL and four other facilities for the Department of Energy, the Center will be housed in the Health and Safety Research Division.

Environmental restoration is a principal concern of the new center. Many health and environmental problems of major national or international significance also fall within the scope of the center's work, as well as issues related to radionuclides, toxic chemicals, acid deposition, and climate change and the

policy and management mechanisms to reduce their adverse impact.

Drawing on the expertise of basic researchers within the ORNL divisions, the center will emphasize the integration of science into decision-making. Examples of activities to be actively pursued by the center include environmental fate/transport modeling, human and environmental toxicology, epidemiology, applied ecology, environmental monitoring, data base development risk/benefit, and policy analysis. In addition to developing methods and performing assessments, the center will provide technical assistance to sponsors responsible for performing or interpreting risk assessments and for managing societal risks.

Curtis C. Travis has been named director of the center. Lawrence W. Barnthouse will serve as the deputy director. The center's management will report to David E. Reichle, ORNL associate director for Environmental, Life and Social Sciences.

The center will solicit scientific associates from all ORNL divisions active in risk-related research and application.

"The Center is designed to increase communications between scientists working in different divisions and programs and ensure that risk assessments and analysis performed for all sponsors meet the highest possible standards of technical excellence," Travis said. "We also want to provide a common focus for marketing a laboratory-level initiative in risk assessment, analysis and management and assure the prior application of technical, social, and political input into our assessments."

The center will also promote training and educational initiatives aimed at professionals in the field and the public, and establish Martin Marietta Energy Systems as a national leader in the area of risk assessment, Travis said.

EPA Enters Into New Data Base To Enhance Information on Innovative Technologies

In an effort to make current information on innovative treatment more widely available, EPA recently announced it will enter into a new data base—the Vendor Information System for Innovative Treatment Technologies (VISITT)—which the Agency will make available to the public in early 1992. The purpose of the database is to increase communication between suppliers of innovative treatment and professionals involved in hazardous waste cleanup. EPA has invited vendors of innovative technologies to submit information on their capabilities for use in the data base. New vendors who meet EPA's criteria and submit a completed forms by September 30, 1991, will be eligible for inclusion in the first release of the database. VISITT will contain information on vendors that treat groundwater in place, soil, sludge, sediments, and solid wastes. Examples of included technologies are soil washing, thermal desorption, bioremediation, solvent extraction, and *in situ* vitrification. EPA wil not include more established technologies, such as incineration, solidification/stabilization, and traditional pump-and-treat for groundwater. The database will be available on computer diskette, and updated at least annually. Vendors must verify or update submitted information at least once a year to remain in the database. Further information is available from the VISITT Hotline: 1-800-245-4505. Forms for vendors to submit can be obtained from EPA's Office of Research and Development, Publications, at 513-569-7562.

Washington Environmental Newsletter

Setting Environmental Priorities:
The Debate About Risk

The latest edition of the *EPA Journal* addresses the debate about the role of risk assessment in setting the nation's environmental priorities. The debate centers around whether Congress and the EPA should rely more on science in setting these priorities. Specifically, should they use comparative risk analysis, assessing and comparing the risks between different problems, as the yardstick? Do we really know enough about risk and is the science adequate?

Last fall, EPA Administrator William K. Reilly used the occasion of the public release of an important and provocative report to launch a national debate on these questions. The report was prepared by EPA's Science Advisory Board at Reilly's request. Among other things the Board recommended applying comparative risk analysis to sort out environmental problems and reevaluate their importance relative to each other.

The *EPA Journal* extended this debate by inviting contributions from some senators and congressmen, who have authority over environmental legislation and appropriations, and asked scientists from universities and government. Additionally they solicited views of knowledgeable representatives from industry and from environmental organizations. AIChE, through its Government Programs Steering Committee submitted a Commentary entitled "The Use of Risk Assessment in Regulatory Rule Making" and is currently updating the paper for submission to Congress and EPA. The Editors of the *Journal* have said that they were impressed by the thoughtfulness and the variety of the responses received, regardless of whether the respondents were skeptical or supportive of risk-based decision making.

Setting environmental priorities for the whole nation and bringing EPA resources into alignment with these priorities is an extremely difficult task, yet in 1991 EPA has a budget of more than $6 billion and employs about 17,000 scientists, lawyers, engineers and other professionals and administrative personnel—a 310 percent increase from the 5,500-person workforce that formed the Agency in 1970. These employees, located in EPA's Washington headquarters, 10 regional offices and 56 research laboratories, work under the authority of a dozen environmental laws and some 100 other statues—all of them enacted since 1970. They are responsible for writing, refining, and enforcing 9,000 regulations and for responding to a annual flood of tens of thousands of letters from Congress, other government officials and taxpayers. Imposing rules of logic, efficiency and effectiveness on this huge bureaucracy will require a keen sense of priorities.

Reilly has said that there is a need for change in EPA's approach to environmental problems, and although important progress has been made over the past two decades, environmental policies have been developed piecemeal, with each problem addressed separately and without sufficient reference to other problems or to overall effects, risks and costs.

AIChE's Government Programs Steering Committee (GPSC) has long urged EPA to rethink its procedures that establish goals on a pollutant-by-pollutant and medium-by-medium basis without adequate consideration of broader environmental quality objectives. Rarely has EPA evaluated the relative importance of pollutants or media—(air, land, and water), nor did they assess the combined impacts on whole ecosystems or human health. The Advisory Committee report and the subsequent debate on the value and efficiency of risk evaluation should create significant changes in the way we look at environmental problems.

The Risk Assessment of Environmental and Human Health Hazards: A Textbook of Case Studies by Dennis J. Paustenbach, John Wiley & Sons, New York, NY, (1989), 1155 pages, [ISBN No.: 0471-84998-7] U.S. List Price: $130.00

Much concern has been expressed over the adverse health and environmental effects associated with a wide variety of personal and environmental exposures. As a result, numerous federal laws have been passed to protect public health and the environment. The responsibility for deciding which substances merit regulatory control and how restrictive these controls should be rests with a number of federal agencies. As such, health and environmental risk assessment has become a major activity of the government and is often a prerequisite to its regulatory decision-making.

Dr. Paustenbach's textbook contains contributions from approximately 50 authors from more than a dozen scientific disciplines and provides a wealth of information for practitioners as well as students of health and environmental risk assessment. The book is divided into eight major sections which include: (1) Basic Principles, (2) Assessing Water Contaminants, (3) Assessing Hazardous Waste Sites, (4) Assessing Air Contaminants, (5) Assessing Occupational Hazards, (6) Assessing Potential Hazards to Consumers, (7) Assessing the Risks to Wildlife, and (8) Risk Management. As the title indicates, this is a textbook of case histories. Many of the chapters are based on work that was originally conducted to satisfy some regulatory requirement or litigation challenge. The authors, in general, take the reader through the entire assessment process and identify limitations to past and current methods. Because of the diverse nature of the authors' experience, I have found this book to be quite useful as a lead into the literature on subject areas that were peripheral to my own.

The book, however, is not without its faults. Although each chapter is extensively referenced, they have not been carefully checked to ensure the correct citation is given. Several times I have attempted to locate a reference, only to be disappointed because it was not to be found where indicated. Also, Chapter 6 on Superfund risk assessments is outdated. EPA's Superfund Public Health Evaluation methodology cited was replaced in September 1989 by the *Risk Assessment Guidance for Superfund, Volume I: Human Health Evaluation Manual*, which incorporates several major changes in the assessment process (for example, selection of indicator chemicals). Lastly, some of the chapters indicate sources of uncertainty or limitations in the current methods only to proceed with the assessment using these same assumptions or methods. Furthermore, little insight is provided for reducing the uncertainty in assessing environmental and human health hazards from the limitations in the current methods. Nevertheless, I recommend this book as a useful addition to the library of practitioners and students of environmental and human health hazards.

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Environmental Chemistry and Toxicology of Aluminum by Timothy E. Lewis, Lewis Publishers, Inc., Chelsea, MI, (1989), 344 pages, [ISBN No.: 0-87371-194-7], U.S. List Price: $69.95

This book is based on technical papers presented in a three-day symposium held at the 194th National Meeting of the American Chemical Society (ACS) held in New Orleans, LA, in September 1987. The symposium, entitled "The Environmental Chemistry of Aluminum" was sponsored by the U.S. Environmental Protection Agency and the Environmental Chemistry Division of ACS. The chapters contained in this book provide a broad overview of the sources, transport, and fate of aluminum in the environment. All the papers were peer-reviewed by at least two scientists knowledgeable in the particular subject area. The editor notes that not all of the papers were suitable for publication following the peer review process; and were, therefore, not included in the book.

The book begins with a two-page introduction and is followed by 19 chapters on various subjects relating to the sources, transport and fate of aluminum in the environment. The chapters were written by people who are very knowledgeable in this field. Aluminum is the most abundant metal and is the third most abundant element, comprising about 8% of the earth's crust. Aluminum occurs only in the oxidized form, Al(III). In solution, aluminum ion hydrolyzes surrounding water molecules, forming hydroxo complexes and decrease the solution pH. Aluminum forms many inorganic and organic complexes in soil and water environments.

Topics covered in the book include: coordination chemistry/Al(III) speciation in aqueous solution; speciation methods for partitioning mononuclear and polynuclear aluminum; stability of aluminum species; modeling interactions of aluminum species, protons, and calcium ions with humic substances in acidic waters and soils; chemistry and transfer of aluminum in forested water-sheds; aluminum levels in subsurface drinking water supplies for prediction of impact by acidic deposition; chemical speciation and plant toxicity; dynamic properties of calmodulin in response to aluminum; episodic variation in streamwater aluminum chemistry; aluminum chemistry of acidic sandy soils; aluminum speciation and organic carbons in surface waters; chronic no-observed effect concentrations of aluminum for brook trout; effects of aluminum in food supplies; chemistry of neurologically active, neutral, and water-soluble aluminum complexes; neurotoxicity of aluminum; and possible counteractive steps in aluminum-dependent encephalopathies. The graphics contained in these chapters are well done, and the references are current (at the time of the writing of the book).

The book contains a wealth of information on the chemical speciation and toxicity effects of aluminum in water supplies. It is an excellent reference source for water treatment specialists, water chemistry scientists, environmental engineers, and toxicologists.

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Fine Pore Aeration for Wastewater Treatment. Pollution Technology Review No. 191, by W. C. Boyle, G. T. Daigger, J. A. Heidman, G. L. Huibregste, J. J. Marx, J. J. McKeown, B. Newbry, T. C. Rooney, L. A. Rossman, G. Speirs, H. D. Stensel, Noyes Data Corporation, Park Ridge, NJ, (1990), 296 pages, [ISBN No.: 0-8155-1252-X], U.S. List Price: $45.00

Supplying oxygen for aeration is an energy intensive process and is the single largest energy consuming operation at activated sludge wastewater treatment plants. The energy consumption represents 50 to 90% of the total wastewater treatment plant's energy requirements. Replacing less efficient aeration systems with more effective ones employing fine pore aeration can save upwards to 50% of the aeration energy costs resulting in simple payback periods of 2 to 6 years. Today there are in excess of 1,300 municipal and industrial wastewater treatment plants in the U.S. and Canada which employ fine pore aeration. Fine pore diffusers include: porous ceramic plates, discs, domes, and tubes; rigid porous plastic plates, discs, and tubes; nonrigid porous plastic tubes; and perforated membrane tubes and discs.

This book contains eight chapters, beginning with an introduction section which provides the historical overview and objectives of the book. The primary objective is to provide the technical community with current information regarding fine pore aeration systems.

Fine pore diffuser characteristics is addressed in chapter two. Topics covered in this chapter include types of fine pore media and diffusers, diffuser layout, characteristics of fine pore media, and clean water performance. Process water performance is covered in chapter three. Factors affecting performance, diffuser fouling, and process water data bases are discussed in this chapter.

Operation and maintenance (O&M) is discussed in chapter four of fine pore aeration systems, while chapter five addresses system design and installation. Topics covered in that chapter include: process and O&M considerations, process oxygen and mixing requirements, air diffuser system and air supply system design, and concludes with a summary of an aeration system design procedure.

Chapter six is concerned with aeration control. Topics covered include the benefits associated with aeration control, control strategy development, and control system components. An example is provided for an aeration control system. The chapter also discusses several experiences (in a case history format) with automated aeration control.

Economic analysis of fine pore aeration systems is covered in chapter seven and chapter eight describes several case histories. Six appendices are provided at the end of the book. The first appendix provides abstracts of contractor studies on a Fine Pore Aeration Project with the U.S. Environmental Protection Agency and the American Society of Civil Engineers. The second appendix describes selected diffuser characteristics and cleaning methods. The third appendix presents selected physical and chemical data, while the fourth appendix presents an economic analysis spreadsheet. The remaining two appendices present symbols, terms, acronyms, and conversion factors.

This publication provides a very good summary and overview of fine pore aeration systems. It is recommended for process designers, end

users, environmental engineers, and regulatory personnel. It provides considerable information on fine pore aeration devices and their performance and operation, along with O&M requirements. The book presents current information for the selection, design, operation, maintenance, and control of fine pore aeration systems.

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Dangerous Properties of Industrial Materials, 7th Edition (a three-volume set), by N. Irving Sax and Richard J. Lewis, Jr., Van Nostrand Reinhold, New York, NY, (1989), Volume I: 756 pages
ISBN No.: 0-442-31910-3,
Volume II: 1706 pages
ISBN No.: 0-442-31811-1,
Volume III: 1821 pages
ISBN No.: 0-442-31813-8,
3-Volume Set:
ISBN No.: 0-442-28020-3,
U.S. List Price (3-volume set):
$375.00

These reference books provide a very comprehensive compendium of toxicological data for more than 20,000 chemical compounds. The first volume contains essays on various hazardous materials topics, a cross-index of CAS registry numbers, a synonym cross-index, and a list of CODEN bibliographic references given in the data sections. Section 1 addresses general toxicology. Section 2 discusses industrial and environmental risks from carcinogens. The history and current mutagenicity testing procedures are discussed in Section 3. Section 4 contains the CAS Number cross-index for the nearly 16,000 CAS numbers of listed materials. The primary name and synonym cross-index are given in Section 5. Section 6 contains the complete CODEN bibliographic references for nearly 2,200 entries. Volumes II (compounds beginning with

letters A through E) and III (compounds beginning with letters F through Z) describe in excess of 20,000 materials, all listed in alphabetical order.

The toxicological data information presented for each compound includes the following: entry name, hazard ranking, CAS Registry Number, access number to the Registry of Toxic Effects of Chemical Substances, DOT classification code; molecular formula, molecular weight, structural formula, properties, synonyms, skin and eye irritation data, mutation data, toxicity dose data, reproduction effects data, carcinogenic effects data, references cited, standards, and toxic and hazard reviews. The properties include a physical description of the material (including form, color, and odor), plus the following information if available: boiling point, melting point, density, vapor pressure, vapor density, refractive index, flash point, autoignition temperature, and the lower and upper explosive limits. Description of exposure are expressed in terms of the following: the lowest dose (TDL_0) required to produce a toxic effect in humans or produce carcinogenic, neoplastigenic, or teratogenic effects in animals or humans; the lowest concentration of materials in air (TCL_0) to which humans or animals have been exposed for any given period of time that produces any effect as described for TDL_0; the Lethal Dose Fifty (LD_{50}) which is a calculated dose of the materials that is expected to cause the death of 50% of an entire defined experimental animal population; and the Lethal Concentration Fifty (LC_{50}) which is a calculated concentration of a material in air for which exposure for a specified period of time is expected to cause the death of 50% of an entire defined experimental animal population. Such toxicity data are provided (along with the reference citations for this data) for animal species such as: humans and infants, rats, mice, hamsters, gerbils, guinea pigs, rabbits, chickens, wild bird species, pigeons, ducks, quail, cats, dogs, frogs, cattle, and monkeys.

This publication provides a very comprehensive set of toxicological data for many chemical compounds and is an extremely valuable reference source. I highly recommend the three-volume set of books as a reference for obtaining quality data at one's finger-tips regarding physical/chemical properties and toxicological data. This edition is a worthwhile investment for people involved in hazardous wastes, risk assessments, site assessments, and toxicology.

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Solvent Waste Reduction, Pollution Technology Review No. 193, U.S. Environmental Protection Agency and ICF Consulting Associates, Inc., Noyes Data Corporation, Park Ridge, NJ, (1990), 158 pages, [ISBN No.: 0-8155-1254-6], U.S. List Price: $45.00

Waste reduction involves any in-plant practice or process that avoids, eliminates, or reduces waste with the purpose of reducing environmental risk to any media. It also includes the treatment, reuse, or recycling of any material that reduces the volume and/or toxicity of wastes prior to final disposition.

Nearly all industrial facilities use solvents for such purposes as cleaning, degreasing, painting, paint stripping, or extraction. It is incumbent upon generators of waste to institute waste reduction programs. After the waste has been minimized, recycling becomes the most appropriate alternative. Other treatment options include incineration, chemical and biological treatment, landfilling, and deep-well injection. Recycling is a very attractive option, because it minimizes the quantity of waste requiring handling and it further conserves our natural resources. For solvents the recycled solvent becomes a useable product.

This book is based on technical papers which were presented at U.S. EPA seminars covering aspects such as solvent waste reduction, from regulations and disposal bans, to on-site and off-site treatment methods. The book contains 14 chapters written by a set of authors knowledgeable in the subject area. Topics covered in the book include: land and liquid disposal bans; SARA Title III (Community Right-to-Know); solvent waste burning regulations; waste minimization liability; minimization of process equipment and cleaning wastes; source reduction for parts-cleaning; solvent waste minimization in the coatings industry; regulations, management, and disposal; chlorinated solvent waste reduction; on-site reuse and recycle of solvents; commercial off-site solvent reclamation; and treatment of solvents and spent solvent waste streams.

Three appendices are included in the publication. The first addresses separation techniques for solvent recovery. The second deals with treatment and pretreatment techniques, while the third describes good operating practices.

The book presents a good overview of the subject. It contains a lot of useful information relating to waste reduction of solvents. The book is a useful reference for environmental engineers, plant engineers, design engineers, plant operators, and waste minimization coordinators.

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Pollution Prevention Program at the University of Rhode Island

Stanley M. Barnett

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The Chemical Engineering Department program at the University of Rhode Island provides special emphasis in process engineering as part of the fundamental principles in chemical engineering. With that kind of training, the students, both graduate and undergraduate, are bringing much needed skills in attacking the twin industrial problems of waste reduction and pollution prevention. The students are the technical key to the successful partnership of the State of Rhode Island's Department of Environmental Management, Rhode Island's industry and the University's Chemical Engineering Department—all working to reduce waste and improve our environment.

This three-way partnership started work in the fall of 1989. The program, funded by the EPA, is a nonregulatory, voluntary, confidential, and cooperative effort to reduce industrial hazardous waste by cost-effective methods. So far, work at forty different company plants has had excellent results. In every instance, at least one cost-effective method for waste reduction was identified and recommended. Thirteen recommendations were made for one plant.

The way the program works is quite simple. An engineer with extensive industrial experience meets with company owners and staff to explain the program. If the company wishes to proceed, the company personnel assemble data on waste streams, including waste shipping manifests, safety data sheets, flow rates, and compositions of process streams, costs, etc. Teams of environmental scientists from RI DEM and URI chemical engineers working side-by-side review the data. Many times the data are full of gaps and questions. The team, lead by an experienced engineer and working with plant personnel, visit the plant as often as needed to get material balances, accurate process flow sheet data and costs. Then the chemical engineers consider process options. Commonly, this can include separation processes to recover and reuse valuable components in the waste streams. Typical options can include ion exchange, dialysis, ultrafiltration or using alternate materials, particularly for hazardous wasters. Costs studies are made and optimum technical and cost recommendations are assembled. Process flow sheets are prepared and a written report is discussed with the company. Essentially,

the technical work and cost studies are done by the students. Their work is reviewed by chemical engineers experienced in industry and by the Chairman, Chemical Engineering Department. Often the report recommends development and testing work leading to final parameter definitions. That kind of work, directed by students, is underway at URI and normally six to ten factory locations.

The companies reviewed so far are diverse in nature. The smallest plant has three employees; the largest sixteen hundred. Company personnel are often not technically prepared to solve pollution problems and welcome the service offered by URI. Product lines include textiles, plating, metal fabrication, high-volume piece manufacturing, auto body shops, coating (urethane) formulators, etc. Most often, the product lines are those of mature industries.

Some results so far are obvious. Proven processes are available to companies to reduce wastes and cost concomitantly. Typically, waste streams can be reduced by fifty to ninety-nine percent. Industry, academia and the government can work together cooperatively and voluntarily to solve severe pollution problems. It is primarily the students who makes the program work on the factory floors. They are the ones who define the real-world changes needed. The program benefits the students as well as industry. The experience of working side-by-side with industry and government representatives is uniquely valuable. The students get paid. A sophomore chemical engineering student, with some guidance, can visit a plant, identify waste streams and find options for reducing waste. A senior can redesign processes and conduct developmental testing on lab and production scale. Two recent graduates, with interest generated in the field, have accepted positions with chemical companies to work in the environmental area.

URI's Chemical Engineering Department is now firmly organized for this work. Faculty members are actively involved. Seven students have been part of the program including a Ph.D. candidate. The State of Rhode Island recently designated the Chemical Engineering Department as the Rhode Island Center for Hazardous Waste Reduction.

To the editor:

With reference to the paper by Herzog, Golomb and S. Zemba, [*Environmental Progress* 10, 64-74 (1991)], in which they claim our calculations of reduced power plant efficiency for CO_2 removal in an integrated power plant is erroneous is just not well founded. In the publication by M. Steinberg, H. C. Cheng and F. Horne, "A System Study for Removal, Recovery and Disposal of Carbon Dioxide from Fossil Fuel Power Plants in the U.S.", [BNL 35666, (May 1984)] and "A Study on the Systematic Control of CO_2 Emissions from Fossil Fuel Power Plants in the U.S., [*Environmental Progress, 5*, 245-255 (November 1986)], we have already estimated the amount of steam taken from the backend of the turbine to be used in the MEA stripper for CO_2 recovery which reduces the thermal efficiency for electrical power production proportional to the steam thermal energy extracted. We did not assume the same thermal efficiency of 38% as Herzog et al. claim we did. Furthermore, using primary coal in a nonintegrated plant to produce steam separately for recovery of CO_2 is much less efficient than using backend turbine steam. We do not see why existing turbines cannot be retrofitted to extract steam for use in the CO_2 control system and condensing the steam in the amine reboiler thus taking advantage of the latent heat of condensation. Also, our estimates indicate that MEA scrubbing is somewhat less energy intensive than air separation and recycling CO_2 for burning coal in oxygen diluted with CO_2. Liquefying and disposing of the CO_2 in the ocean will reduce power plant efficiency by another 4% resulting in a total efficiency loss of at least 7%. The net efficiency of the plant is then reduced from 38 to 31% which is in the same order as the reduction of thermal efficiency from 34.4% to 27.8% estimated by EPRI for an

IGCC plant [W. G. Snyder and C. A. Depew, EPRI, AP 4827 (1986)].

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Reply:

In regard to Dr. Steinberg's letter, we stand by our original analysis. We agree that an integrated, cogeneration approach is more energy efficient than the nonintegrated case for amine scrubbing which was presented in our paper [*Environmental Progress* 10, 64-74 (Feb. 1991)]. However, we disagree that an integrated amine scrubbing approach is less energy intensive than an air separation/flue gas recycling process for CO_2 capture.

The heart of this disagreement is the calculations presented in Appendix B of M. Steinberg, H. C. Cheng, and F. Horn, "A System Study for the Removal, Recovery, and Disposal of CO_2 from Fossil Fuel Power Plants in the U.S.," [DOE/CH00016-2, U.S. Dept. of Energy, Dec. (1984)]. The thermal efficiency of the integrated plant was estimated by using a heat balance to prorate a base case power plant's 38% thermal efficiency:

$$E = 0.38 \times [Q - Q_b/(\eta_1 \times \eta_2)]/Q \quad (1)$$

where E = power plant efficiency
Q = fuel heating value in Btu/ton CO_2
η_1 = boiler efficiency
η_2 = reboiler efficiency
Q_b = turbine heat loss due to low pressure steam extraction

and Q_b can be represented as:

$$Q_b = Q_a(h_A - h_B)/(h_A - h_C) \quad (2)$$

where Q_a = the reboiler heat requirement
h_A = the enthalpy of low pressure steam
h_B = the enthalpy of output steam from the turbine
h_C = enthalpy of output flow from the reboiler.

Steinberg, et al. use the following values:

Q = 9.81×10^6 Btu/ton CO_2 (based on coal)
η_1 = 90%
η_2 = 85%
Q_a = 4.8×10^6 Btu/ton CO_2
h_A = 1227.4 Btu/lb (100 psia, 400°F)
h_B = 1096.4 Btu/lb (0.5 psia, 80°F)
h_C = 196.27 Btu/lb (20 psia, saturated liquid)

For several reasons, we feel that Steinberg et al.'s use of equation (1) is incorrect. To illustrate our point, let's take the extreme case where the total boiler effluent is required by the amine stripper reboiler, that is, $Q_a = Q \eta_1 \eta_2$. Using their values for Q, η_1, and η_2, this corresponds to $Q_a = 7.5 \times 10^6$ Btu/ton CO_2. With the total boiler effluent going to the amine stripper reboiler, no steam is available for the turbine, thus the power plant thermal efficiency is 0%. However, following Steinberg, et al.'s calculational method using equation (1) we would obtain a power plant efficiency of 33.2%!

The above reasoning prompted us to examine their work in more detail. We have three major objections to their method:

(1) While Equation (1) is correct for the nonintegrated plant where steam is extracted directly from the boiler, we can find no theoretical basis for applying it to an integrated, cogeneration power plant.
(2) This procedure does not check steam mass balances. That

means for large values of Q_a (which we have), the low pressure steam requirement defined as $Q_a/(h_A - h_C)$ can be larger than the total steam flow.

(3) No second law requirements are considered. This leads to overoptimistic values for h_A, h_B, and h_C. Specifically,

- The low pressure steam at 100 psia will have a significantly higher temperature than 400°F, raising h_A.
- The turbine outlet will have some condensate, lowering h_B.
- The reboiler outlet will need to be greater than 20 psia, raising h_C.

To correctly analyze the cogeneration case, the thermodynamics of the power cycle must be modeled rigorously. This was done in a recent joint study by the Electric Power Research Institute (EPRI) and Fluor Daniel, Inc. (see Smelser, et al., "An Engineering and Economic Evaluation of CO_2 Removal from Fossil Fuel-Fired Power Plants," EPRI report IE 7365 (June, 1991)). For an integrated amine scrubbing power plant, the EPRI/Fluor Daniel study predicted a 25% reduction in power exclusive of CO_2 compression (a thermal efficiency reduction from 34.8% to 26.2%) compared to a reduction of 8% (from 38.0 to 34.9%) based on Steinberg, et al.'s procedure.

Concerning the use of existing turbines, Smelser, et al. comment "In developing the retrofit plant design, an investigation was made into extracting low pressure steam from the existing turbine for this service. About 40% of the total steam flow in the plant is required at full load. This amount of steam cannot be extracted from the existing turbine because, according to General Electric, allowable turbine blade design stresses would be exceeded". Practically speaking, retrofitting an existing turbine by steam extraction would almost never be economically attractive even if all technical design and operating issues were resolvable.

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Use of Electronic Bulletin Boards for Environmental Management

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As a result of changes to existing environmental protection legislation, and the numerous changes to existing regulations that continually take place, environmental managers need updated information on federally mandated programs and regulations, approved and other mathematical models, control technologies, acceptable measurement techniques and continuing education courses. The United States Environmental Protection Agency (EPA) is providing help to state and local air pollution control agencies, the regulated community, consultants and the general public through electronic bulletin boards. Each bulletin board (BB) uses data base management systems and communication technology to provide access to information on several specific topics of interest to the environmental manager. The purpose of this review is to discuss 9 bulletin board systems (BBS) (see Table I) available to the public from the EPA [1, 2, 3, 4]. Several alternative bulletin board systems are also available and will be discussed in future columns.

A brief description of the 9 BBSs is given in the following paragraphs.

ATTIC System: The Alternative Treatment Technology Information Center (ATTIC) provides technical information and data on alternative methods for treating hazardous waste. The data have been obtained from literature searches, case histories, treatability data bases, transport and fate data bases and expert systems (for example, Geophysics Advisor Expert System). The ATTIC data base contains abstracts and executive summaries of over 1,400 technical documents. All the documents are in keyword searchable format.

Five major categories of treatment are included in the data base to classify technologies. The categories are defined as follows:

Thermal
Including rotary kiln incineration, fluidized bed combustion, infrared incineration, pyrolysis, and plasma heat systems

Biological
Including aerobic and anaerobic treatment, composting, biodegradation, and microbial degradation processes

Solidification/Stabilization
Including cement-based fixation, pozzolonic-based fixation, and vitrification processes

Chemical
Including oxidation-reduction reactions such as ozonation, alkaline chlorination, electrolytic oxidation, and chemical dechlorination

Physical
Including absorption, distillation, and filtration processes

State and local agencies plus the general public can access the BBS through both the ATTIC system operator and an on-

Table 1 Partial list of available Bulletin Board Systems from the EPA

Name	Description
APTI*	Courses available from Air Pollution Training Institute
ATTIC	Information on available innovative hazardous waste site treatment technologies
CAAA*	Current information on Clean Air Act Amendments of 1990
CHIEF*	Tools for estimating air pollutant emissions
EMTIC*	Emission measurement technical information on stationary sources
NSR	New Source Review guidance and technical information
SCRAM*	Air quality models and meteorological data for regulatory work
VISITT	Current information on innovative treatment technologies

*Available on OAQPS-TTN bulletin board system

The views expressed in this article are solely those of the authors.

line computer system. The user must, however, register to use the ATTIC system by answering a series of questions at the time of the first phone call (telephone # is 301-670-3808). The remote system should be configured to emulate a VT-100 terminal, using 8 data bits, 1 stop bit, and no parity. A users manual will be available soon from the EPA. Other capabilities of the system are:

(1) Bulletin Board—to provide news bulletins and information on conferences.
(2) Message Center—to communicate with other system users and with the system operator.
(3) File Transfer—to download files to your personal computer via standard transfer protocols (for example, xmodem).

NSR System: The new source review (NSR) bulletin board is designed for providing up-to-date NSR guidance and technical information to state and local agencies and the general public.

The NSR bulletin board provides facilities for downloading/reading the full text of recent guidance and policy material, viewing summaries of past guidance material and soliciting/providing information to others related to new source permitting. The NSR bulletin board also allows the user to access the clearinghouse for best available control technology (BACT) and lowest achievable emission rate (LAER).

A user can register by contacting Jo Ann Allman of the New Source Review Section, EPA (Telephone # 919-541-5591). For the effective use of the NSR bulletin board, the user is required to obtain a copy of a remote terminal access software pc ANYWHERE III (ATERM) from any local computer store.

VISITT: Vendor Information System for Innovative Treatment Technologies (VISITT) is being developed by the EPA to provide information on vendors of innovative technologies to treat soils, sludges, sediments and groundwater *in situ*. The system will include information submitted by manufacturers, developers and suppliers of innovative treatment technology equipment and services. The system will also help hazardous waste cleanup professionals. The plan is to create a file for each vendor which includes the company name, address, contacts, phone number and description of the treatment technology. The description will include the advantages and limitations of the technology, and the types of contaminants and wastes to which it is applicable.

The system will allow the user to enter a waste description, a specific technology and/or a specific cleanup site to bring up relevant information. A user will then be able to view the information and can choose to print the desired information on vendor/technology. The Vendor Information Form (EPA/540/2-91/011) is available from the EPA by calling 501-569-7562.

OAQPS TTN Bulletin Board Systems: The EPA Office of Air Quality Planning and Standards (OAQPS) has developed a technology transfer network (TTN) BBS for the use of air quality scientists throughout the world.

The OAQPS TTN includes 6 BBSs: SCRAM, CHIEF, APTI, EMTIC, CAAA and CTC. The last one, Control Technology Center (CTC) BB is being developed to provide assistance in control technology and emission source assessments. The user can register by calling 919-541-5742. The following communication setup is required: 8 data bits, no parity, 1 stop bit and 1200 or 2400 baud.

SCRAM System: A complete description of the Support Center for Regulatory Air Models (SCRAM) was given in an earlier column by Kumar and Mohan [4]. The system is designed to provide information on air quality models used by federal, state and local agencies. A user is allowed to download the models for his/her applications.

CHIEF System: The Clearinghouse for Inventories and Emission Factors (CHIEF) is a BBS that is useful to anyone interested in or working in the area of emissions estimation and development of air emission inventories. CHIEF serves as a central clearinghouse for the latest information on air emission inventories and emission factors based on the AP-42 manual and its updates. This BB also includes an emission estimation data base, and provides access to newsletters, announcements and guidance on performing inventories. CHIEF is accessed through the OAQPS-TTN. The following files can be downloaded from CHIEF for your work:

SPECIATE—Speciation factors for both volatile organic compounds and particulate matter are included. The profiles are listed by profile name and by source classification code.
XATEF—Air toxic emission factors are included in the file. The emission factors are searched by source descriptions and pollutant.
SIMS—The Surface Impoundment Modeling System (SIMS) is used for estimating air emissions from wastewater collection devices and surface impoundments.
AFSEF—This file contains information on Source Classification codes and Emission Factor listing.

APTI System: Also available on the OAQPS-TTN system is information on the training and courses offered through the Air Pollution Training Institute (APTI). APTI, funded by the EPA, offers the widest scope of air pollution on training in the United States, develops instructional material and provides technical assistance to training activities conducted in support of regulatory programs related to air pollution abatement.

APTI materials are used in EPA sponsored lecture and laboratory courses scheduled at several locations in the U.S. Individual training is provided through self-instructional courses. APTI training materials and courses are continually updated. APTI publishes a "Chronological Schedule of Air Pollution Training Courses" each year describing the training offered with a description of courses offered and how to obtain the training.

Information on course types, course curriculum, registration, course schedule, examinations and training publications is available on the bulletin board.

EMTIC System: The Emission Measurement Technical Information Center (EMTIC) bulletin board system is available to users seeking technical guidance on emission testing issues related to stationary sources. The EMTIC system is particularly aimed at professionals who conduct and/or oversee emissions tests to support the development of emission standards, emission factors and state implementation plans.

This system provides detailed information on approved EPA methods applicable to each stationary source category, citations to source documents, alternatives to the test methods and limitations. The EMTIC system is accessed through the OAQPS-TIN.

CAAA System: The Clean Air Act Amendments (CAAA) Bulletin Board System should be of interest to all air quality professionals, regulators at all levels, the regulated community and the general public. The system allows access to information on the Clean Air Act Amendments of 1990, making the task of understanding, implementing and complying with the new requirements easier. The complex nature of the 1990 Amend-

ments, with its numerous deadlines and requirements, shall prove to be very useful for users of this system. The CAA BB can be accessed through OAQPS-TTN.

We were able to register and access ATTIC, OAQPS TTN, SCRAM, CHIEF, APTI, and CAAA bulletin boards with considerable ease and encountered no problems in their use. All the BBS are user friendly. It is our understanding that the above BBSs can be accessed from anywhere in the world.

Bulletin Board Systems are helpful tools in day-to-day environmental management work. They provide an economical means to obtain the latest information on various aspects of one's work. Interactions with other scientists and managers are becoming increasingly easier with commuter communications through the various EPA BBSs. At the University of Toledo, environmental engineering students are able to use the BBS to complete some of their classroom assignments. Very soon we will start wondering how we ever managed our work without a BBS. We are confident that you will find the BBSs described here useful in your daily work; and that regular use will help you stay informed and current.

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Temperature Profile and Heat Transfer Model For a Chemical Wastewater Treatment Plant

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This paper presents a heat transfer model for equalization, activated sludge, and trickling filter unit processes that can be used to assess the effect of operating temperature on unit process selection, materials of construction selection, and heat retention and cooling requirements. In developing this model, the individual variables that affect the operating temperature of biological systems were first identified. Mathematical relationships were then developed to describe system behavior, based on conservation laws and rate equations. The heat transfer models were then used to develop a temperature profile of the two alternative WWTP configurations.

INTRODUCTION

A chemical facility in the Northeast generates high-strength, high-temperature process wastewater which is treated biologically in surface impoundments equipped with high-speed floating aerators. Historically, the wastewater treatment plant (WWTP) has experienced performance problems during cold temperature operation. With the regulatory trend toward more stringent effluent limits and better performance, two retrofit options for upgrading the existing WWTP were considered: (1) an above-ground equalization tank followed by a single-stage activated sludge treatment system and, (2) an above-ground equalization tank followed by a two-stage trickling filtration/activated sludge system. The historical cold weather performance problems made temperature control an important design parameter. Between 285 K and 310 K, biological treatment systems can operate very effectively. In the upper temperature range, sludge yields are lower, oxygen demands higher, and soluble organic removal efficiencies higher. At lower-range temperatures, oxygen demand is lower, sludge yields higher, and soluble organic removal efficiencies lower. Temperatures outside the optimal range can create operational problems,

including poor soluble organic removal at lower temperatures and excessive solids carryover at higher temperatures.

Previous heat transfer models examined heat transfer from an in-ground basin [1]. In this case, a model was needed for heat transfer from systems in above-ground open tanks. Existing equations were modified and new equations developed for this application.

A heat balance model was prepared to predict operating temperatures during winter and summer conditions for both alternatives. The impact of construction material on heat loss was also evaluated.

HEAT TRANSFER MODELS

Equalization Tank and Activated Sludge System

To develop the heat transfer model, the law of conservation of energy was used. If the kinetic energy, potential energy, and shaft work contributions to the law of conservation of energy equation are neglected, the following equation is obtained:

FIGURE 1. Summary of heat gain and loss terms.

$$\Delta H = Q_t \qquad (1)$$

where

ΔH = enthalpy change between the effluent stream(s) and influent stream(s), J/hr
Q_t = net heat gain or loss, J/hr

Figure 1 shows a typical above-ground open tank and the associated means of heat transfer. To calculate the enthalpy change between the influent and the effluent streams, the following equations are used:

$$\Delta H = H_{out} - H_{in} \qquad (2)$$

$$H_{in} = \Sigma[\dot{m}c_p(T_{in} - T_{ref})] \qquad (3)$$

$$H_{out} = \Sigma[\dot{m}c_p(T_w - T_{ref})] \qquad (4)$$

where

ΔH = enthalpy change between the outlet stream(s) and inlet stream(s), J/hr
H_{in} = enthalpy of influent stream(s), J/hr
H_{out} = enthalpy of effluent stream(s), J/hr
$\dot{m}$ = mass flow rate of wastewater, kg/hr
c_p = heat capacity of wastewater, J/kg/K
T_{in} = temperature of influent stream(s), K
T_w = temperature of wastewater in tank, K
T_{ref} = reference temperature, K

The heat transfer gains and losses (J/hr) associated with this system are as follows:

$$Q_t = Q_r + Q_e + Q_{ct} + Q_{cw} + Q_{cg} + Q_a + Q_m + Q_s + Q_b \qquad (5)$$

where

Q_t = net heat gain or loss
Q_r = radiant heat
Q_e = evaporative heat
Q_{ct} = convective heat through tank wall
Q_{cw} = convective heat through water surface
Q_{cg} = conductive heat (ground)

Q_a = aeration heat
Q_m = mechanical heat
Q_s = solar heat
Q_b = biological heat

The general heat transfer terms applicable for the equalization tank and activated sludge system net heat gain or loss term, Q_t, must be determined. This is done by determining whether specific heat transfer terms apply for specific processes. As an example, the aeration heat transfer term, Q_a, would apply only for heat transfer from an aerated tank.

For an equalization tank, the net heat gain or loss equation reduces to

$$Q_t = Q_r + Q_e + Q_{ct} + Q_{cw} + Q_{cg} + Q_m + Q_s \qquad (6)$$

For a diffused air activated sludge system, the net heat gain or loss equation reduces to

$$Q_t = Q_r + Q_e + Q_{ct} + Q_{cw} + Q_{cg} + Q_a + Q_m + Q_s + Q_b \qquad (7)$$

Expressions are then obtained for the equalization tank or the activated sludge system models by combining equation (6) or (7) with equation (1). Once the input parameters (e.g., system configuration, ambient condition) are taken into account, the only unknown is T_w, the wastewater temperature.

The resulting equation can be solved for T_w numerically or by trial and error. A trial and error solution is arrived at by assuming a value for T_w and solving for Q_t and ΔH. The correct effluent wastewater temperature is that which makes $\Delta H = Q_t$.

Radiant heat losses, Q_r, can be estimated as follows [1]:

$$Q_r = 0.2041 \times 10^{-3}[A_{wall}\epsilon_{wall}T_{wall}^4 - T_{amb}^4)$$
$$+ A_s\epsilon_{water}(T_w^4 - T_{amb}^4)] \qquad (8)$$

where

A_{wall} = tank wall surface area, m^2
ϵ_{wall} = emissivity of tank wall, dimensionless
T_{wall} = tank wall temperature, K
T_{amb} = ambient temperature, K
A_s = exposed liquid surface area, m^2
ϵ_{water} = emissivity of water, dimensionless

To estimate the outer wall temperature of the tank, the following equations can be used, assuming negligible resistance to heat transfer from the liquid film on the tank wall [2]:

$$T_{wall} = T_w - \frac{(x_w/k_m)(d_i/d_{log})(\Delta T)}{(x_w/k_m)(d_i/d_{log}) + (1/h_o)} \qquad (9)$$

$$d_{log} = \frac{d_o - d_i}{\ln(d_o/d_i)} \qquad (10)$$

where

T_{wall} = outer surface tank wall temperature, K
T_w = wastewater temperature, K
x_w = wall thickness, m
k_m = thermal conductivity of tank, J/m/s/K
d_i = inside tank diameter, m
d_o = outside tank diameter, m
ΔT = difference between the wastewater temperature and the ambient temperature, K
d_{log} = log-mean diameter, m
h_o = air film heat transfer coefficient, J/m/s/K

The term (d_i/d_{log}) is a correction factor used for heat transfer from a cylinder. When dealing with heat transfer from a flat wall (as would be the case when analyzing heat transfer from a rectangular aeration tank), this term should be omitted.

Evaporative heat losses, Q_e, can be estimated as follows [1]:

$$Q_e = -\left[199,745\left(1 - \frac{RH}{100}\right) + 11,967(T_w - T_{amb})\right]$$
$$* \exp[0.0604(T_{amb} - 273)] V_w A_s^{0.96} \quad (11)$$

where

RH = relative humidity, percent
T_w = wastewater temperature, K
T_{amb} = ambient temperature, K
V_w = wind velocity, m/s
A_s = exposed liquid surface area, m^2

Convective heat losses through tank wall, Q_{ct}, can be estimated as follows [1]:

$$Q_{ct} = -3600 U_A A_{wall}(T_w - T_{amb}) \quad (12)$$

where

U_A = overall heat transfer coefficient for wall, $J/m^2/s/K$
A_{wall} = tank wall surface area, m^2
T_w = temperature of wastewater, K
T_{amb} = ambient temperature, K

Convective heat losses through water surface, Q_{cw}, can be estimated as follows [1]:

$$Q_{cw} = -20,585(T_w - T_{amb}) V_w A_s^{0.95} \quad (13)$$

where

T_w = temperature of wastewater, K
T_{amb} = ambient temperature, K
V_w = wind velocity, m/s
A_s = exposed liquid surface area, m^2

Conductive heat losses to the ground, Q_{cg}, can be estimated as follows [1]:

$$Q_{cg} = -3600 U_g A (T_w - T_g) \quad (14)$$

where

U_g = overall heat transfer coefficient for heat conduction to the ground, $J/m^2/s/K$
A = surface area of tank bottom, K
T_w = wastewater temperature, K
T_g = average ground temperature, K

Diffused air aeration heat losses, Q_a, can be estimated as follows [1]:

$$Q_a = -(F_{air})[4.522 \times 10^6(T_w - T_{amb})$$
$$+ 4.401 \times 10^6 \exp(0.0604[T_{amb} - 273])\left(1 - \frac{RH}{100}\right)$$
$$+ 2.638 \times 10^6 \exp(0.0604[T_{amb} - 273])(T_w - T_{amb})] \quad (15)$$

where

F_{air} = air flow rate, m^3/s
T_w = wastewater temperature, K
T_{amb} = ambient temperature, K
RH = relative humidity, percent

If the heat loss due to mechanical aeration needs to be considered, equation (15) can easily by modified. Reference [1] offers more details.

Mechanical heat gain, Q_m, can be estimated as follows:

$$Q_m = (P)\left(\frac{m_e}{100}\right)\left(\frac{r_e}{100}\right)(3600) \quad (16)$$

where

P = power, W
m_e = motor efficiency, percent
r_e = mechanical efficiency, percent

Solar heat gain, Q_s, can be estimated as follows [3]:

$$Q_s = 3600 A_s E_b (\sin \alpha) \exp(-n a_{ms} m)\beta \quad (17)$$

$$\alpha = \pi/2 - WWTP \text{ Latitude} \quad (18)$$

$$m = csc \alpha \quad (19)$$

$$a_{ms} = 0.128 - 0.054 \log m \quad (20)$$

where

E_b = solar flux (1,394 $J/m^2/s$)
α = solar angle, rad
m = relative thickness of air mass, dimensionless
n = turbidity factor of air, dimensionless
a_{ms} = molecular scattering coefficient, dimensionless
A_s = exposed liquid surface area, m^2
β = solar angle correction factor, dimensionless

In this paper, the value of n is 3. This represents a moderately smoggy day. The value of n can be adjusted depending upon the atmospheric conditions.

Biological heat gain, Q_b, can be estimated as follows [4]:

$$Q_b = 3600 R_b \text{ COD}_r(1 - 1.48 Y_{obs}) \quad (21)$$

where

R_b = amount of heat released per unit mass of COD removed, J/kg COD
COD_r = rate of COD removed by biological activity, kg COD/s
Y_{obs} = observed biological yield, kg volatile suspended solids (VSS) produced/kg COD removed
1.48 = COD/VSS ratio for biomass, kg COD/kg VSS

If a wastewater contains only one primary organic constituent, R_b can be calculated using that constituent's heat of combustion. For acetic acid (heat of combustion equals 873 kJ/g-mole [5], and theoretical COD equals 1.07 kg COD/kg acetic acid [6]) this value is 1.359×10^4 kJ/kg. If there is more than one primary organic constituent, a mass-weighted term for R_b must be developed.

Y_{obs} is also a function of temperature and solids retention time as follows:

$$Y_{obs} = \frac{Y_T}{1 + b_h \theta_c} \quad (22)$$

$$b_h = b_{ho}\theta_T^{(T_w - 293)} \quad (23)$$

where

Y_T = true yield, kg VSS produced/kg COD removed
b_h = decay coefficient, $days^{-1}$
T_w = wastewater temperature, K
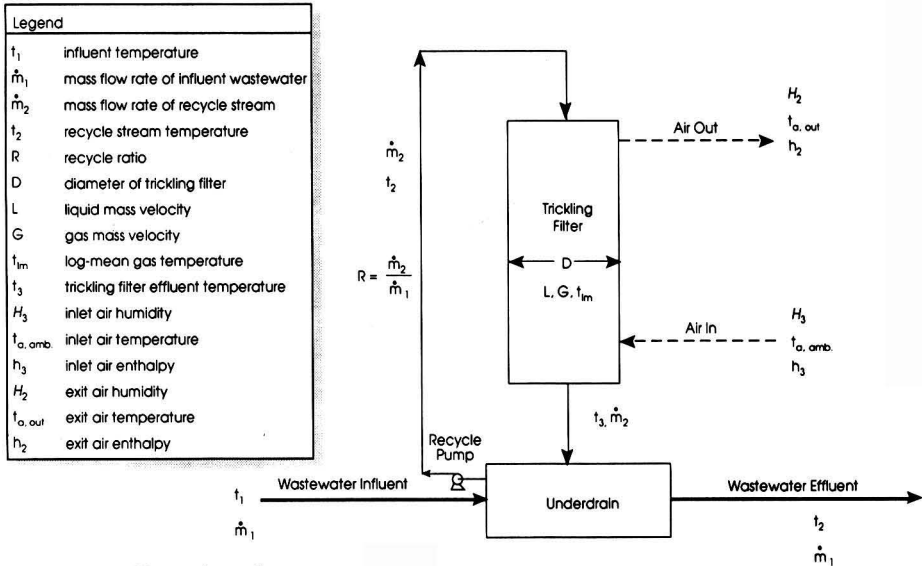
FIGURE 2. Trickling filter schematic.

θ_c = solids retention time, days
b_{ho} = decay coefficient at 293 K, days^{-1}
θ_T = temperature activity coefficient, dimensionless

Trickling Filters

To analyze the heat loss from the trickling filters (Figure 2), it was necessary first to calculate the enthalpy change in bone-dry air (BDA) flowing through the trickling filter. The following equation was used:

$$\Delta h_{\text{air ent.}} = |h_3 - h_2| \qquad (24)$$

where

$\Delta h_{\text{air ent.}}$ = change in the actual air enthalpy across the trickling filter, J/kg BDA
h_3 = enthalpy of ambient air entering the bottom of the trickling filter, J/kg BDA
h_2 = enthalpy of air leaving the top of the trickling filter, J/kg BDA

Before the entering and exiting air enthalpies were calculated, the following assumptions were made:

a. The air leaving the trickling filter is saturated with water.
b. The temperature of the air leaving the trickling filter is halfway between that of the inlet air and water [7].

To calculate the entering and exiting air enthalpies, the following equations were used [5, 8]:

$$\log_{10}(p^*/133.3) = 8.10765 - 1750.286/[(t_a - 273) + 235] \qquad (25)$$

$$RH = (p/p^*) \times 100 \qquad (26)$$

$$H = (18/29)(p/(101,325 - p)) \qquad (27)$$

$$c_s = (0.24 + 0.45H) \times 4186.8 \qquad (28)$$

$$h = c_s(t_a - 255) + 2.467 \times 10^6 H \qquad (29)$$

where

p^* = vapor pressure of water at t_a, pascals
t_a = air temperature, K
p = partial pressure of water at t_a, pascals
RH = relative humidity of air at t_a, percent
H = humidity of air, kg H_2O/kg BDA

Table 1 Dimensions (in feet) of Proposed WWTP Alternatives				
Unit Process	Parameter	Alternative 1	Alternative 2
Equalization Tank (1)	Diameter	152	152
	Sidewall Depth	30	30
	Wall Thickness	2	2
Trickling Filters (4)	Diameter	—	65
	Height	—	21
Aeration Tank (1)	Length	284	284
	Width	142	142
	Height	22	22
	Wall Thickness	2	2

1 foot = 0.3048 m

Table 2 Parameters Used in Heat Balance Model

Parameter and Units	Variable	Summer	Winter	Reference
Emissivity of Wall, dimensionless	ϵ_{wall}	0.63	0.63	11
Emissivity of Water, dimensionless	ϵ_{water}	0.96	0.96	11
Mass Flow Rate of Wastewater, lb/hr	$\dot{m}$	8.9×10^5	8.9×10^5	
Mass Flow Rate of Wastewater into Underdrain, lb/hr	$\dot{m}_1$	2.2×10^5	2.2×10^5	
Recycle Ratio, dimensionless	R	5	5	
Ambient Temperature, °F	T_{amb}	48	12	12
Relative Humidity, percent	RH	70	58	12
Air Film Heat Transfer Coefficient, Btu/ft²/hr/°F	h_o	0.2	0.2	13
Thermal Conductivity, Btu/ft/hr/°F	k_m	0.64	0.64	11
Wind Velocity, m/s	V_w	3.1	4.1	12
Overall Heat Transfer Coefficient for Wall, Btu/ft²/hr/°F	U_A	2	2	14
Overall Heat Transfer Coefficient for Conduction to Ground, Btu/ft²/hr/°F	U_g	0.55	0.55	15
Ground Temperature, °F	T_g	60	60	15
Air Flow Rate, m³/s	F_{air}	9.9	9.9	
Mechanical Power (mixers), hp	P	120	120	
Motor Efficiency (mixers), percent	m_e	87	87	
Mechanical Efficiency (mixers), percent	r_e	95	95	
Mechanical Power (blowers), hp	hp	1,326	1,326	
Motor Efficiency (blowers), percent	m_e	95	95	
Mechanical Efficiency (blowers), percent	r_e	75	75	
Solar Angle, degrees	$\propto$	53	53	
Solar Angle Correction Factor, dimensionless	β	$\pi/4$	$\pi/4$	
Relative Thickness of Air Mass, dimensionless	m	1.25	1.25	3
Turbidity Factor, dimensionless	n	3	3	3
Molecular Scattering Coefficient, dimensionless	a_{ms}	0.123	0.123	3
Solar Flux, Btu/hr/ft²	E_b	442	442	3
COD Removal Rate, lb COD/hr	COD$_r$	2,083	2,083	
True Yield, lb VSS produced/lb COD removed	Y_T	0.27	0.27	
Solids Retention Time, days	θ_c	23	23	
Decay Coefficient at 293K, days^{-1}	b_{ho}	0.07	0.07	
Temperature Activity Coefficient, dimensionless	θ_T	1.02	1.02	16
Porosity, dimensionless	τ	0.94	0.04	4

1 lb = 0.4536 kg
$t_K = (t_F + 459.67)/1.8$
1 Btu/ft²/hr/°F = 5.678 J/m²/s/K
1 hp = 745.6 W
1 W = 1 J/s
1 degree = $(\pi/180)$ rad
1 Btu/ft/hr/°F = 1.731 J/m/s/K

c_s = humid heat capacity of air, J/kg BDA/K
h = enthalpy of airstream, J/kg BDA

Grady and Lim [9] suggest that cooling tower correlations and approximations can be used to calculate heat losses from trickling filters. Using this assumption, the equation is:

$$\Delta h_{air\ ent.} = \Delta h_{op.\ line} \tag{30}$$

where

$\Delta h_{air\ ent.}$ = change in the actual air enthalpy across the trickling filter, J/kg BDA
$\Delta h_{op.\ line}$ = enthalpy change in the air using the operating line equation, J/kg BDA

In the design of a cooling tower, the relationship between the approximate bulk characteristics of the liquid and gas phases is desired. This relationship is obtained by a mass balance and is called an operating line. The operating line of a cooling tower is an expression that shows the relationship between the
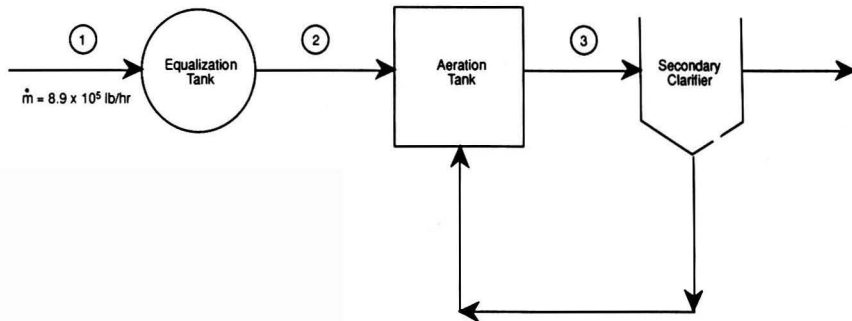
Condition	Ambient Temperature (°K)	Relative Humidity (%)	Stream Temperature (°K) 1	2	3
Summer	282	70	333	327	322
Winter	262	58	305	301	302

1 lb. = 0.4536 kg

FIGURE 3. Alternative 1—single-stage activated sludge.

water temperature and the enthalpy of the air. Thus, by using the cooling tower equation, a relationship can be found between the enthalpy of the air leaving the cooling tower and the entering water temperature.

To use the operating line equation for estimating heat losses from trickling filters, the following assumptions must be made:

- The gas velocity of air in the trickling filter is constant at 10 ft/min [10]. This value was chosen because temperatures at the trickling filter recycle water inlet and exit corresponded to the temperatures observed during pilot testing.
- The gas velocity can then be used to calculate the gas mass velocity of BDA as follows:

$$G = 300 V \rho \tau \tag{31}$$

where

G = gas mass velocity, kg BDA/s/m^2
V = gas velocity of BDA, m/s
ρ = density of BDA, kg/m^3
τ = porosity, dimensionless

- Likewise, the liquid mass velocity can be calculated as follows:

$$L = 3600 \dot{m}_2 / A_t \tag{32}$$

$$A_t = \pi D^2 / 4 \tag{33}$$

where

L = liquid mass velocity, kg H$_2$O/s/m^2
$\dot{m}_2$ = mass flow rate of H$_2$O in recycle stream, kg H$_2$O/s
A_t = cross sectional area of trickling filter, m^2

- The ratio Lc_p/G is constant throughout the trickling filter.
- The effects of all other heat losses are negligible.
- The density of the air in the trickling filter can be calculated from the log-mean temperature of the inlet and exit air temperatures as follows [4]:

$$t_{lm} = \frac{t_{a, \, out} - t_{a, \, amb}}{\ln(t_{a, \, out}/t_{a, \, amb})} \tag{34}$$

where

t_{lm} = log-mean temperature of air in the trickling filter, K
$t_{a, \, out}$ = exit air temperature, K
$t_{a, \, amb}$ = ambient temperature, K

Once these assumptions are made, the operating line equation can be used to estimate the enthalpy change in the air. The operating line equation is [8]:

$$\Delta h_{op.line} = (Lc_p/G)_{op} (t_2 - t_3) \tag{35}$$

where

$\Delta h_{op.line}$ = enthalpy change in the air as the wastewater cools from t_2 to t_3, J/kg BDA
L = liquid mass velocity, kg H$_2$O/s/m^2
c_p = heat capacity of wastewater, (4186 J/kg/K)
G = gas mass velocity, kg BDA/s/m^2
t_2 = temperature of wastewater entering trickling filter, K
t_3 = temperature and wastewater leaving trickling filter, K

To calculate t_3, and thus t_2, a relationship between these two temperatures is needed. This relationship can be obtained by using an energy balance around the underdrain to obtain t_2 as a function of t_3.

It was assumed the liquid in the underdrain was well-mixed. This indicated the trickling filter effluent temperature would be equivalent to that of the recycle stream. To estimate t_2, the following equation was used, assuming all other heat losses were negligible:

$$t_2 = t_r + [\dot{m}_1 c_p (t_1 - t_r) + \dot{m}_2 c_p (t_3 - t_r)]/[(\dot{m}_1 + \dot{m}_2) c_p] \tag{36}$$

where
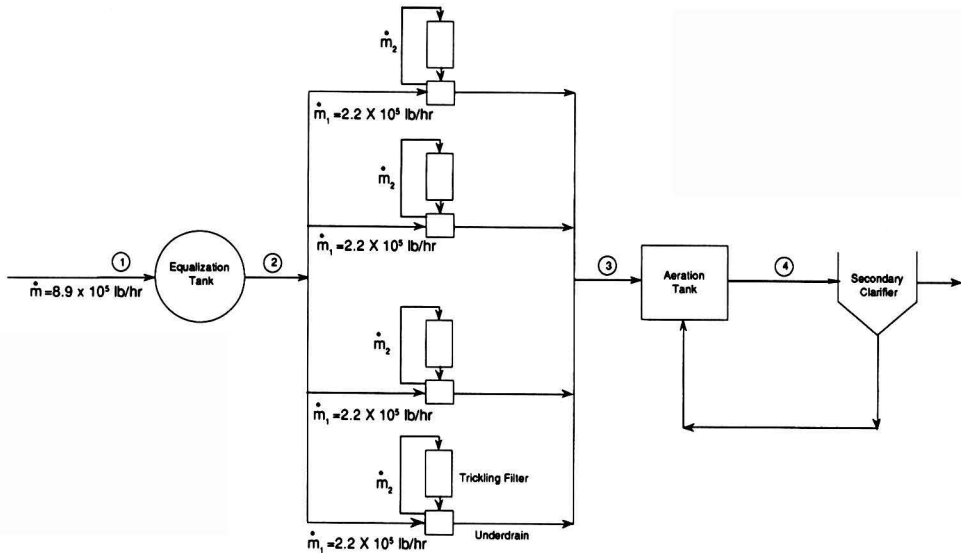
Condition	Ambient Temperature (°K)	Relative Humidity (%)	Trickling Filter Recycle Ratio	Trickling Filter Air Velocity (ft/min.)	Stream Temperature (°K)			
					1	2	3	4
Summer	282	70	5:1	10	333	327	318	316
Winter	262	58	5:1	10	305	301	297	299

1 ft. = 0.3048m
1 lb. = 0.4536 kg

FIGURE 4. Alternative 2—Trickling filter/activated sludge alternative.

$\dot{m}_1$ = mass flow rate of wastewater entering underdrain, kg/s
c_p = heat capacity of wastewater, 4186 J/kg/K
t_1 = temperature of wastewater entering underdrain, K
t_r = reference temperature, K
$\dot{m}_2$ = mass flow rate of wastewater entering trickling filter, kg/s
t_3 = assumed temperature of wastewater leaving trickling filter, K

DISCUSSION

Two WWTP alternatives were evaluated using the heat transfer model:
- Alternative 1—Single-Stage Activated Sludge
  —Equalization
  —Activated Sludge
- Alternative 2—Two-Stage Activated Sludge
  —Equalization
  —Trickling Filtration
  —Activated Sludge

Table 1 presents the unit process dimensions for both alternatives. Table 2 shows the parameters used in the heat balance model.

Figures 3 and 4 show the temperature profile of each alternative. For alternative 1, the aeration tank temperature may reach 322 K during the summer; therefore, wastewater cooling is needed. During the winter, the aeration tank temperature will be 301 K, which is above the 285 K minimum needed for biological treatment. For alternative 2, the summer temperature of wastewater entering the trickling filters and the aeration tank will be above 310 K, resulting in the need for cooling. The winter temperatures of wastewater entering the trickling

filters and aeration tank would be 301 K and 297 K, respectively, which are within the optimum range for biological treatment.

Table 3 presents the individual heat gains and losses for both options. For alternative 1, the greatest heat gain is in the aeration tank from biological activity. The control options are influent cooling or aeration tank cooling. In this case, aeration tank cooling is best because the biological heat will be released in the aeration tank. Aeration tank cooling offers greater temperature control than influent cooling. Figure 5 illustrates the aeration tank cooling concept.

For alternative 2, Table 3 shows that the greatest heat loss is due to evaporation at the trickling filters. The greatest heat gain is again from biological activity. For this alternative, the only control option is influent cooling before the trickling filters, because the temperature of the wastewater flowing over the trickling filters must be below 310 K. Figure 6 illustrates this option. The wastewater cooling system is positioned after the equalization tank to decrease the response time of the control variable (aeration tank temperature).

For alternative 1 with cooling, the aeration basin operates at a higher temperature (310 K) than alternative 2 with cooling 307 K. Alternative 1 would have lower yields and higher oxygen uptake rates. Aeration tank cooling provides greater temperature control due to the inherent temperature variability of influent wastewater.

Table 4 shows the temperature gradients across the walls of the unit processes. These temperature differences provide the driving force for heat losses through the tank walls. Careful selection of construction materals (e.g., concrete vs. steel, tank insulation) can minimize these losses. Thermal stresses must be carefully considered.

Table 3 Summary of Heat Transfer Parameters for Alternatives 1 and 2

Heat Transfer Parameter	Equalization Tank (Alternatives 1 and 2)		Trickling Filter (Alternative 2)		Aeration Tank (Alternative 1)		Aeration Tank with Trickling Filters (Alternative 2)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
Radiant Heat	(2,100,000)	(1,400,000)	—	—	(3,600,000)	(2,900,000)	(3,000,000)	(2,600,000)
Evaporative Heat	(3,600,000)	(1,400,000)	—	—	(9,900,000)	(3,000,000)	(8,600,000)	(2,700,000)
Convective Heat (Wall)	(2,300,000)	(2,000,000)	—	—	(2,700,000)	(2,700,000)	(2,300,000)	(2,700,000)
Convective Heat (Water)	(3,200,000)	(3,700,000)	—	—	(8,100,000)	(7,800,000)	(6,900,000)	(7,100,000)
Conductive Heat (Ground)	(700,000)	(200,000)	—	—	(1,300,000)	(500,000)	(1,100,000)	(400,000)
Aeration Heat	—	—	—	—	(3,700,000)	(2,300,000)	(3,100,000)	(2,100,000)
Mechanical Heat	300,000	300,000	—	—	2,300,000	2,300,000	2,300,000	2,300,000
Solar Heat	3,200,000	3,200,000	—	—	7,000,000	7,000,000	7,000,000	7,000,000
Biological Heat	—	—	—	—	11,700,000	11,200,000	11,600,000	11,200,000
Evaporative Heat (Trickling Filters)	—	—	(14,400,000)	(7,200,000)	—	—	—	—

Note: Numbers in parentheses are negative values
1 Btu = 1055 J

CONCLUSIONS

1. Since WWTP performance is affected by operating temperature, temperature control is a critical design factor.

2. Modeling is recommended to determine temperature profiles through a WWTP. These models should consider all heat transfer parameters.

3. Heat losses are greater from the trickling filters/activated sludge system than from the activated sludge alone.

4. Biological heat gain can be significant and should be considered in any heat balance for a WWTP.

5. Evaporative and convective heat losses have the most significant impact on wastewater cooling. Both will always be present, but can be controlled. Evaporative losses can be minimized by process selection (e.g., activated sludge rather than trickling filters/activated sludge). The impact of heat losses can be evaluated; these can be reduced by carefully selecting construction materials.
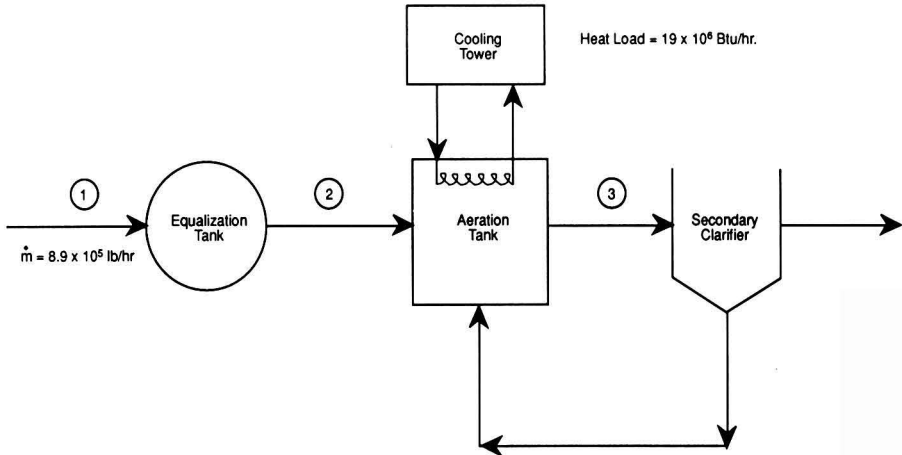
Condition	Ambient Temperature (°K)	Relative Humidity (%)	Stream Temperature (°K) 1	2	3
Summer	282	70	333	327	310

1 lb. = 0.4536 kg
1 Btu = 1055 J

FIGURE 5. Alternative 1—single-stage activated sludge with aeration tank cooling.
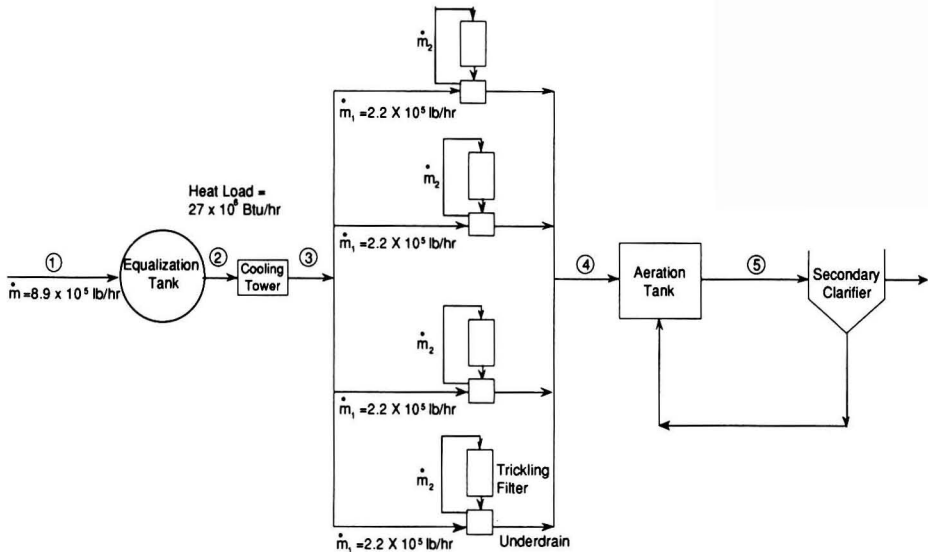
FIGURE 6. Alternative 2—Trickling filter/activated sludge alternative with influent cooling.

Condition	Ambient Temperature (°K)	Relative Humidity (%)	Trickling Filter Recycle Ratio	Trickling Filter Air Velocity (ft/min.)	Stream Temperature (°K)				
					1	2	3	4	5
Summer	282	70	5:1	10	333	327	310	305	307

1 lb. = 0.4536 kg
1 ft. = 0.3048 m
1 Btu = 1055 J

Table 4 Temperature Gradients for WWTP Examples

Unit Process	Difference between Wastewater Temperature and Outer Wall Temperature, K	
	Summer	Winter
Equalization Tank	18	16
Aeration Tank (with trickling filters)	13	14
Aeration Tank (without trickling filters)	16	15

6. Activated sludge systems can effectively be cooled in the aeration tank.

7. Cooling is required for the trickling filter/activated sludge system to protect the trickling filter from high temperature wastewater. This will result in lower operating temperatures in the downstream aeration tank.

8. After the system heat balance is performed, heat retention and cooling requirements can be matched to the operating requirements of individual unit processes.

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Legal Incentives for Minimizing Waste

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Waste minimization, or pollution prevention, has become an integral component of federal and state environmental regulation. Minimizing waste offers many economic and public relations benefits. In addition, waste minimization efforts can also dramatically reduce potential criminal requirements. This paper addresses the legal incentives for minimizing waste under current and proposed environmental laws and regulations.

INTRODUCTION

Waste minimization, or pollution prevention, has become a popular phrase in today's age of increased environmental regulation and potential liability. The U.S. Environmental Protection Agency (EPA) estimates that $120 billion is spent annually "to treat or contain wastes once they are generated" [1]. Further, the agency states that hazardous waste treatment and disposal costs have risen as much as 300 percent over the past decade due to the ban on land disposal of hazardous waste, minimum technology requirements for hazardous waste units, and limited treatment and disposal capacity [2]. *Ibid.*

Through waste minimization and pollution prevention, EPA anticipates that industrial facilitates can save money on waste management, reduce the use of raw materials, and minimize potential environmental liability [2]. Despite these incentives to minimize waste, corporations are often reluctant to commence waste minimization programs prior to being forced to do so by federal or state government, and incurring substantial criminal and civil penalties. Potential toxic tort and Superfund liabilities can also be substantial.

Legal incentives for waste minimization exist under all major environmental laws, including the Resource Conservation and Recovery Act (RCRA), the Clean Air Act, the Clean Water Act, and Superfund. Moreover, under each of these statutes, there is always the threat of federal, state, and private citizen enforcement actions, as well as potential criminal liability. Penalties under these laws can amount to as much as $25,000 per day for each violation. Needless to say, such penalties can easily result in the assessment of multimillion dollar fines against a company. Furthermore, mandatory jail time has become a stark (and increasingly common) reality for environmental crimes.

As a result of increased environmental liability, companies must reevaluate past waste disposal practices and devise innovative solutions to recover and recycle materials that were previously released or disposed to air, land, or water.

Discussion

Waste Minimization: An Historical Perspective

Waste minimization and pollution prevention have recently captured the attention of EPA and the public. As President Bush announced in October, 1990:

> *Environmental programs that focus on the end of the pipe or the top of the stack, on cleaning up after the damage is done, are no longer adequate. We need new policies, technologies, and processes that prevent or minimize pollution—that stop it from being created in the first place [4].*

As defined by EPA, waste minimization is:

> *The reduction, to the extent feasible, of hazardous waste that is generated prior to treatment storage or disposal of the waste stored or disposed of. It is defined as any source reduction or recycling activity that results in either (1) reduction of total volume or of hazardous waste; (2) reduction of toxicity of hazardous waste; or (3) both, as long as that reduction is consistent with the general goal of minimizing present and future threats to human health and the environment [5].*

With President Bush's recent "mandate" in place, EPA is now attempting to move to the forefront of the waste minimization and pollution prevention arena. However, waste minimization goals have been around for a number of years.

Waste minimization was first introduced as a national policy in the 1984 Hazardous and Solid Waste Amendments (HSWA) to RCRA. Despite this professed waste minimization policy, however, only a few regulations force industry to minimize waste.

RCRA provides a prime example of the absence of mandatory waste minimization provisions. HSWA endorses a waste

minimization policy and, in that spirit, requires hazardous waste generators to have programs in place to reduce the volume and toxicity of their waste to the degree economically feasible, and to minimize present and future threats to human health and the environment from treatment, storage, and disposal methods. However, under this provision it is within a company's discretion to determine what level of waste minimization is "economically feasible." In fact, EPA recognizes that this term "is to be defined and determined by the generator and is not subject to subsequent reevaluation by EPA" [6]. Thus, the generator has the flexibility to determine what is economically practical for the generator's circumstances and there is no real mechanism to enforce compliance with RCRA's waste minimization goal [7]. *Ibid.*

In addition to implementing waste minimization programs, RCRA § 3002 (a) (6) requires hazardous waste generators to identify in their biennial reports to EPA (or the State): (1) the efforts undertaken during the year to reduce the volume and toxicity of waste generated; and (2) the changes in volume and toxicity actually achieved in comparison with previous years, to the extent such information is available. Once again, no direct incentives are provided in RCRA to force waste minimization efforts.

Finally, HSWA's land ban had the indirect effect of forcing waste minimization. Specifically, HSWA prohibited land disposal of hazardous wastes that do not meet a specified treatment standard using the best demonstrated available technology. This ban on land disposal caused generators to analyze methods for reducing the volume and/or toxicity of the hazardous waste generated. EPA's recent regulations governing the burning of hazardous waste in boilers and industrial furnaces may have this same indirect effect of minimizing waste [8].

Waste Minimization: Today's Incentives

Although there are few direct regulatory incentives for waste minimization, today's climate of increased criminal and civil liability should encourage a corporate pollution prevention philosophy. If the threat of jail time does not provide a sufficient incentive for minimizing waste, substantial fines, as well as Superfund and toxic tort liability, will attract a corporations's attention.

Criminal Liability

Throughout the eight-year existence of the U.S. Department of Justice's Environmental and National Resources Division, criminal prosecutions for environmental crimes have increased sharply. In all, the Division has successfully sought indictments of 703 defendents — 222 corporations and 481 individuals. A total of 581 convictions resulted — 163 corporations and 354 individuals. Fines alone amounted to over $56 million. Particularly eye-opening is the fact that under federal sentencing guidelines, persons convicted of illegally storing or transporting hazardous wastes will, in most cases, be subject to mandatory prison terms.

Fiscal year 1990 was a record year for criminal enforcement actions. During 1990, EPA referred 375 civil cases and 65 criminal cases to the Justice Department. The Justice Department returned 134 indictments in FY 1990 and achieved a 95 percent conviction rate. More than three quarters of these indictments were against corporations and their top officers. Moreover, in 1990 courts sentenced environmental violators to a total of 745 months in prison, which was reduced to 222 months after suspension of sentences. According to the Justice Department, more than half of the individuals convicted last year for environmental crimes were given prison sentences, with about three quarters of those persons serving jail time, which averaged more than a year. Aside from prison sentences, the Justice Department estimates that fines imposed for en-

vironmental crimes rose to a record $30 million in FY 1990, up from $12.7 million in FY 1989 [9].

The following provide a few examples of this dramatic trend in criminal enforcement for environmental violations:

1. The president of a California hazardous waste management company was sentenced December 3, 1990 to six months in jail and fined $28,000 for illegally storing and transporting hazardous waste in violation of RCRA [10].
2. In a Clean Water Act criminal case, a Massachusetts metal finishing company president was sentenced November 11, 1990 to serve 26 months in prison, placed on two years probation, and ordered to pay a $400,000 fine. His company was fined $50,000 and ordered to pay insurance premiums for two employees exposed to toxic levels of nitric acid, nitrogen dioxide, and nickel. Both the president and the company were convicted in May 1990 of illegally discharging nickel plating wastes and nitric acid from the company's metal finishing operations to the public sewer system [11].
3. On November 16, 1990 the Weyerhaeuser Company pleaded guilty to criminal charges and agreed to pay $500,000 for discharging paint wastes and wash water into a river in violation of the Clean Water Act [12].
4. On November 5, 1990, a Kentucky company and its president were indicted on eleven counts of violating the Safe Drinking Water Act. They were charged with willfully constructing and operating five underground injection wells to inject fluids into an underground drinking water source without obtaining a permit. If found guilty, the president faces a maximum jail sentence of 35 years and a $2.75 million penalty. The company could be fined up to $5.5 million [13].

Civil Liability

In addition to the record criminal prosecution during FY 1990, the Justice Department had the largest ever total civil penalty assessments, amounting to $32 million, with the largest single civil penalty being assessed against Texas Eastern Pipeline Company, which was fined $15 million.

Under most environmental statutes, civil penalties can be assessed up to $25,000 per day per violation. EPA is making a concerted effort to increase civil penalties. Penalties should be sufficient to reflect the gravity of past violations, deter noncompliance, and eliminate economic incentives to violate the law. The following represent some cases studies of both litigated and settled environmental cases brought by both government and private citizens:

1. Public Interest Research Group of New Jersey (NJPIRG) filed a Clean Water Act citizen suit against Powell Duffryn Terminals, a bulk chemical storage facility, in 1984. After 5 years of litigation, the federal district court assessed a record $3.2 million dollar penalty. The court concluded that the maximum penalty that could be assessed against Powell Duffryn was $4.2 million, but because the State had aquiesced in Powell Duffryn's noncompliance, the court reduced that maximum amount by $1 million. On appeal, the Third Circuit held that the district court's $1 million reduction was improper—in other words, even if the State agrees that a facility is doing the best that it can in controlling pollution, if a permit is violated, no reliance can be made on state nonfeasance [14].
2. In a RCRA action, a citizen's group intervened in an action brought by EPA, claiming that Environmental Waste Control's (EWC) operation of a hazardous waste landfill violated several aspects of RCRA. After concluding that the company was liable because it had vi-

olated the statue, the court calculated a maximum penalty of over $60 million. Finding this amount to be excessive, however, the court reduced the penalty to $2,778,000. The court also issued an injunction permanently closing the landfill, a remedy which the citizen's group, not EPA, had sought [15].

3. Exxon recently settled a Clean Water Act citizen suit alleging violations of Exxon's wastewater discharge permit at the Company's Bayonne, New Jersey facility. In this case, two citizen groups provided Exxon with 60 days' notice of their intent to file a Clean Water Act citizen suit. During that 60-day period, Exxon installed a granulated activated carbon unit, which greatly improved Exxon's discharge. Despite Exxon's good faith attempts to minimize pollutants in its wastewater discharge, the citizen groups filed suit. Under the terms of the settlement agreement, Exxon agreed to invest $2,845,000 for environmentally beneficial mitigation projects at the Bayonne facility. In this connection, Exxon agreed to spend $1,850,000 to install dome roofs on fifteen petroleum product storage tanks and to spend $995,000 for the design and implementation of a petroleum product collection system at the facility's barge pier to allow further recovery of petroleum products from the facility's wastewater collection system [16].

   In a sense, the Exxon settlement agreement was a "win-win" situation. On the other hand, the citizen suit resulted in minimization of waste discharged to the waterway. In addition, without admitting liability, Exxon agreed to fund environmentally beneficial mitigation projects, instead of risking substantial civil penalties.

4. After almost 6 years of litigation, Union Oil of California recently agreed to a settlement in a Clean Water Act case with the Sierra Club and the State of California requiring Union Oil to make payments totaling $5,550,000. Attorney's fees alone amounted to $1.25 million [17].

States are also becoming more active:

1. The State of Washington recently fined a solvent recycling firm over $900,000. Alleged violations included selling fuel containing hazardous waste, hazardous waste spills resulting in soil and groundwater contamination, exceeding waste storage capacity, failing to report waste received, improper labelling of waste containers, storing flammable waste in violation of fire codes, and improper employee training and spill prevention plans [18].

2. The Monsanto Co. recently agreed to pay a $1 million penalty for illegally disposing untreated wastewater containing hydrochloric acid. The company was also directed to pay an additional $200,000 to a state trust fund [19].

3. In Kentucky, Ashland Petroleum Co. agreed in November 1990 to pay a $750,000 penalty and construct additional emission control equipment costing $65 million to settle claims the company violated state air quality regulations at its Catlettsburg, Kentucky refinery. The $65 million investment includes $15 million to construct an electrostatic precipitator to reduce emissions from the refinery's catalytic cracking unit and a $47 million filter recovery unit to enhance the refinery's ability to minimize sulfur dioxide emissions [20].

Toxic Tort Liability

Liability resulting from toxic tort claims can also be substantial. For example, settlement agreements amounting to over $23 million have been reached between four chemical companies and more than 1200 individuals who claimed injury from dioxin contamination in Times Beach, Missouri [21]. Similarly, in a toxic tort case against Ashland Oil, the jury awarded a $10.3 million judgment to four persons alleging refinery emissions damaged their property and quality of life [22].

Superfund Liability

Superfund costs have also risen dramatically, growing by more than 28 percent in FY 1990. EPA estimates that private companies have agreed to pay $1.3 billion to clean up hazardous waste sites. A total of 151 Superfund cases were filed in 1990, 50 percent more than filed the year before [23]. Also, during FY 1990, EPA referred 79 cases, valued at $185 million, for prosecution to recover agency expenditures. This represents a 30 percent increase over 1989 figures. EPA also issued 131 unilateral administrative orders in FY 1990, up from 100 in 1989 [24].

A few recent examples typify this upward trend. Under a Superfund consent decree filed in federal court in October 1990, a group of 23 companies agreed to pay nearly $3 million for cleaning and monitoring costs at the Lees Cane Landfill Superfund site in Kentucky [25]. Similarly, at Arizona's largest Superfund site, the responsible parties agreed to pay approximately $17.3 million to remove volatile organic compounds from ground water [26]. Finally, to clean up the New Bedford, Massachusetts harbor and for natural resources damages, the Justice Department reached an agreement with three parties requiring them to contribute over $78 million [27].

Minimizing Potential Liability

Because of the threat of significant criminal and civil liability resulting from waste disposal practices, waste minimization incentives are increasing every day.

Statutory Incentives

The Clean Air Act Amendments of 1990. The Clean Air Act Amendments of 1990 provide a significant opportunity for pollution prevention. Specifically, Title III offers credit for early reductions of toxic air emissions and Title IV provides economic incentives for reducing sulfur dioxide and nitrogen oxide emissions. First, under Title III, industrial sources can obtain a six-year extension from compliance with Maximum Achievable Control Technology (MACT) standards if they: (1) achieve reductions of 90 to 95 percent below a baseline year (no earlier than 1987) before such standards are proposed; or (2) enter into enforceable commitments to achieve such reductions by January 1, 1994. Clean Air Act § 112 (i) (5). However, despite this statutory incentive to reduce emissions early, as yet, there are no EPA guidelines on how to establish an appropriate baseline year. Moreover, a source could encounter several problems in establishing an appropriate baseline. First, EPA could contend that the year chosen by the source is not representative of the source's historic emissions. Second, EPA could dispute the methodology that the source used to calculate its emissions. Thus, a source could spend considerable funds attempting to comply with the voluntary reduction provisions only to later have EPA dispute the source's baseline. If EPA prevails, the source could be required to immediately install MACT, even though the source had already drastically reduced emissions. Prior to the issuance of EPA guidance on this issue, it may be advisable to obtain EPA advance approval of the source's baseline emissions.

Emission reductions also exist under Section 112 (i) (6) of the Clean Air Act, as amended. That section provides that if an existing source has installed Best Available Control Technology (BACT) (to comply with Prevention of Significant Deterioration Requirements) or Lowest Achievable Emission Rate

(LAER) (to comply with nonattainment new source review) prior to the promulgation of a standard, then that source's compliance date is extended for five years from the date on which BACT or LAER was installed or the reductions achieved. This exemption acknowledges that BACT and LAER result in substantial emission reductions and that immediately requiring any additional reductions would be inequitable. However, like the 6-year extension of Section 112 (i) (5), this exemption may have limited effect since those pollutants regulated by BACT and LAER will only slightly overlap those regulated by the Air Toxics provision.

In addition to Title III's emission reduction incentives, Title IV incorporates a system of marketable allowances for sulfur dioxide (SO_2) and nitrogen oxide (NO_x) emissions. This system allows sources to market their "extra" emissions reductions (that is, reductions beyond those otherwise required) to other sources seeking to emit more than is permitted. Clean Air Act § 403 (b).

Finally, Section 404 (d) allows the owner or operator of an affected unit under Title IV to petition EPA for a two-year extension of Title IV's 1995 SO_2 emissions reduction deadline. To obtain the two-year extension, the unit must either use a qualifying technology, or transfer its emissions reduction obligation to another unit using a qualifying technology. A qualifying technology is a technological system of continuous emissions reduction that achieves a 90 percent reduction in SO_2 emissions. The NO_x emission limitation for these units will also be extended for two years. Clean Air Act § 407 (a).

SARA § 313. EPA considers the Toxic Release Inventory (TRI) established under Section 313 of the Emergency Planning and Community Right-to-Know Act to be the most powerful tool available to EPA at the present time for tracking pollution prevention efforts from industrial sources. The public accountability fostered by the TRI has also created a strong incentive to minimize waste [28].

Section 313 requires certain manufacturers to report the amount of each of more than 300 toxic chemicals listed in the Act that are released to the air, land, or water. The reporting requirements, which will expand to cover more than 28,000 facilities nationwide for 1989 data, apply to manufacturing plants that employ at least 10 people and use at least 10,000 pounds or manufacture at least 25,000 pounds of any TRI chemical.

Several states are using the TRI as the basis for a number of legislative efforts. Louisiana has a law mandating 50 percent reduction in toxic air emissions by 1994. Massachusetts and Oregon have enacted similar laws. New Jersey now requires firms to submit with their TRI data additional information about pollution prevention practices. Other states have instituted a fee system based on TRI emissions to provide an economic incentive to reduce emissions.

EPA is also using Section 313 violations to force waste minimization and pollution prevention efforts. For example, EPA Region V announced in December 1990 that two manufacturers agreed to install pollution controls in exchange for reduced fines under Section 313. One company agreed to spend $85,000 to incorporate pesticides automatically into the company's fertilizer product in lieu of a manually operated system. The other company agreed to spend over $45,000 to convert from solvent-based to water-based coatings in its plastics manufacturing operations. For both cases, EPA reduced the proposed penalties from a combined $76,000 to just over $21,000 [29].

Pollution Prevention Act of 1990. The Pollution Prevention Act of 1990 requires EPA to develop and implement a strategy to promote pollution prevention. The Act includes provisions directing EPA to set measurable goals, to consider the impact of regulation on source reduction, and to evaluate regulatory and non-regulatory barriers. In addition, the Act amends Section 313 of SARA to require industries to quantify the effect of source reduction, as well as recycling and treatment, in reducing environmental releases of toxic chemicals.

To implement the mandates of the Pollution Prevention Act, EPA is relying on voluntary efforts, which will offer industry the advantage of maximum flexibility, and sufficient time to make economically sound changes in production or use of raw materials [30].

EPA's Pollution Prevention Strategy. EPA's recently issued Pollution Prevention Strategy anticipates that "pollution prevention can be the most effective way to reduce risks by reducing or eliminating pollution at its source" [31]. In EPA's assessment, waste minimization is often the most cost-effective option because it reduces raw material losses, the need for extensive "end of pipe" pollution control technologies, and long-term liability. Thus, EPA concludes that pollution prevention "offers the unique advantage of harmonizing environmental protection with economic efficiency" [32]. *Ibid.*

EPA's Pollution Prevention Strategy identifies two primary goals: (1) investigate and, where possible, eliminate barriers to cost-effective investments in prevention in existing and new regulatory programs; and (2) encourage voluntary actions by industry that reduce the need for EPA to take action.

To institute this program, EPA has devised an Industrial Toxics Project. Specifically, on February 7, 1991, EPA launched a new initiative to prevent toxic chemical pollution [33]. EPA's new initiative requests over 600 designated companies to reduce pollution voluntarily to air, water, and land. The Project targets seventeen chemicals from the manufacturing sector and develops focused prevention strategies for them. EPA's goal is to reduce aggregate environmental releases of these targeted chemicals, as measured by the Toxics Release Inventory in 1988, by 33 percent by the end of 1992 and at least 50 percent by the end of 1995. Although participation in the Industrial Toxics Project is voluntary, EPA will work with companies to ensure that any initiative taken to reduce emissions ahead of statutory schedule receives appropriate credit toward complying with any subsequent regulatory requirements. Furthermore, EPA Administrator Reilly has expressed his commitment to develop the incentives necessary to ensure participation in this Project and to assure companies that voluntary compliance will not result in the forfeiture of various allowances under the new Clean Air Act [34].

Future Regulatory and Liability Incentives

In addition to requesting voluntary compliance with waste minimization efforts, EPA is expected to continue its increased civil and criminal enforcement efforts. EPA's "Great Lakes Initiative" is representative of the types of environmental lawsuits to come. Under this Initiative, the Justice Department filed three suits in federal district court against three companies alleging violations of the Clean Air Act, the Clean Water Act, the Safe Drinking Water Act, and RCRA [35]. These types of suits test the agency's new multi-media, geographic-based approach to environmental law violations.

Also, on February 22, 1991, EPA and the Justice Department filed eight lawsuits and 20 administrative actions to enforce RCRA's restrictions on land disposal of hazardous waste [36]. One of the federal court actions involved a $1.85 million settlement with E. I. DuPont de Nemours Co. [37]. DuPont was charged with unlawful disposal of corrosive acids and solvent wastes, as well as waste analysis and recordkeeping violations. To settle the lawsuit, DuPont agreed to audit company facilities nationwide to ensure compliance with RCRA's land ban restrictions.

While civil and criminal liability will continue to increase, EPA has also requested public comments on ways to revise EPA's regulations to better encourage waste minimization and pollution prevention. In this regard, on October 5, 1990, EPA issued a request for comments on the desirability and feasibility of waste minimization incentives [38]. EPA requested comments on a number of specific issues, which, if implemented by the agency, could dramatically change the nature of current

waste minimization incentives. The following are a few of the specific questions raised by EPA:

Should EPA consider changing the definition of "solid waste" to promote additional source reduction and recycling? Here, EPA is attempting to respond to criticism that EPA's current permitting process is cumbersome, time-consuming, and carries associated regulatory costs and liabilities.

Should EPA consider marketable waste generation trading rights or other long-term economic incentives to reduce waste generation? [*39*] *Ibid.* In this connection, EPA espouses that it could issue rights to generate a limited quantity or toxicity of hazardous waste. EPA sets forth two variations of this alternative. Under the first variation, a facility, in the first year, would receive transferrable rights for the quantity of waste generated during a base period. The next year the facility would receive rights to generate a smaller percentage (e.g., 5% less) and so on over time. If a facility implemented waste minimization efforts which reduced its need for these rights, it could sell them to other firms. Under the second alternative, EPA would allocate waste generation rights without respect to a facility's individual current waste generation rates. To allocate those rights, EPA would hold auctions with companies which have bought the rights being able to trade them to others if they did not need them [*40*]. *Ibid.*

Should EPA consider waste characterization assessment and listing incentives? One potential long-term option focuses on expanding the data collection and analysis portion of the listing process to require collection and dissemination of source reduction and recycling information for processes that generate the waste [*41*]. *Ibid.* Another approach would be to allow generators to enter into an agreement with EPA that provides time for the generator to identify, design, and install source reduction and recycling technologies that will either significantly reduce or eliminate hazardous waste generated [*42*]. *Ibid.*

Should EPA consider waste minimization incentives in the RCRA Treatment, Storage, and Disposal (TSD) permit process? EPA suggests that the agency could include waste minimization commitments as a condition to permit approval. EPA is also analyzing whether to require permittees to submit a waste minimization facility plan either as a condition for issuing a TSD permit, or as a supplement that must be submitted within a certain time frame (e.g., 150 days) following issuance of a permit. The facility plan would include information on the amount and type of hazardous waste generated, identification of the source of waste by waste stream, an analysis of technically and economically feasible hazardous waste reduction techniques, and a program and schedule for implementing feasible reduction techniques [*43*]. *Ibid.*

Should compliance monitoring and enforcement play a greater role in promoting waste minimization? EPA believes that broadened enforcement efforts could promote pollution prevention beyond that achieved by market forces. Specifically, EPA's enforcement settlement process will be used by the agency to implement pollution prevention strategies by incorporating them into settlement agreements. "For example, settlements could require a company to conduct periodic waste audits or to submit a comprehensive analysis of the effect of waste minimization on its operations, or make specific process changes to minimize waste generation" [*44*]. *Ibid.* EPA expects this policy, to take effect in FY 1991, to be applicable to both administrative actions and civil judicial settlements negotiated in conjunction with the U.S. Department of Justice. Specifically, EPA encourages the inclusion of pollution prevention conditions, as either the means of correcting a violation, or as additional conditions incidental to injunctive relief. Such conditions may offer the best chance of avoiding recurring or future violations, without negative cross-media impacts, provided that technologically and economically feasible options exist. EPA notes, however, that civil penalties will continue to be a mandatory component of the agency's settlement policy [*45*].

Conclusion

In sum, the minimization of waste can have significant benefits. Waste reduction and recycling not only save industry money directly through the reduction in raw material usage, but will also minimize potential environmental criminal and civil liability, as well as future Superfund and toxic tort claims. Industry must reanalyze waste generation and disposal so as to minimize future liability. Waste minimization can be accomplished through raw material substitution, product reformulation, process or equipment modification, improved housekeeping, better management practices, and on-site closed loop recycling [*46*].

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Development of a Transportable Thermal Separation Process

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A new process for remediation of organics-contaminated soils and sludges has been developed. The process consists of a soil dryer and a gas separation system. The dryer heats the soil indirectly to 200–450°C in a rotary kiln, volatilizing the water and organic contaminants. No oxygen is present, and no organic destruction or incineration occurs. The dry treated soil discharged from the dryer is used for backfill at the site. The gas separation system condenses and collects the volatilized contaminants. The vapors are first sent to a water spray scrubber to remove the dust, then are cooled with heat exchangers to about 4°C to condense the water and organics. The water is treated and used to wet the cleaned soil or discharged, as appropriate, while the organics are shipped offsite for later treatment. Most of the remaining gas is reheated and recycled to the dryer. The gas not recycled is cleaned and vented. Development has progressed from laboratory and pilot units to a full commercial scale unit capable of processing 115 metric tons per day of soil with 20% moisture. Soil contaminants effectively removed include polychlorinated biphenyls (PCBs), petroleum hydrocarbons and chlorinated hydrocarbons.

INTRODUCTION

Soils and sludges contaminated with organic chemicals are a widespread problem, with millions of cubic meters requiring remediation in the U.S. alone. Clean-up of contaminated soils and sludges is regulation-driven, with the primary regulatory programs including [1]:

- CERCLA — The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (Superfund).
- SARA — The Superfund Amendments and Reauthorization Act of 1986.
- RCRA Corrective Action (RCRA = The Resource Conservation and Recovery Act)
- RCRA Closures.
- Real estate transfers — state by state.

The total cost of this cleanup effort is estimated at over $200 billion over the next 30 or 40 years [1].

A number of processes can be used for treating organics in soils. One of the more popular techniques has been thermal treatment. As of early 1990, over one million tons of contaminated soil and waste had been thermally remediated by twenty thermal treatment service contractors [2]. Thermal treatment can be further classified into: 1) those which employ incineration of the soil, and 2) those which employ thermal desorption. The latter type of processes generally heats the soil no higher than 550°C, most often, but not always, in the absence of oxygen. The organics are volatilized and, in a separate downstream operation, are either destroyed or condensed. Incineration, on the other hand, heats the soil to higher temperatures in an oxidizing atmosphere and volatilizes and combusts the organics simultaneously. Table 1 lists available thermal desorption technologies. Several of the companies listed now offer commercial remediation services.

Chemical Waste Management (CWM) initiated development of its low temperature thermal treatment process, now named X∗TRAX™, in 1987 after laboratory testing by CWM had shown that at the relatively low temperatures of 250–450°C

Table 1   Thermal Separation Processes

Company	Thermal Unit	Capacity of Largest Unit (metric tons/hour)	Comments	Reference
Deutsche Babcock Anlagen AG	Indirect rotary kiln	7	Pretreatment to incinerator	5
TDI Services	Electrically heated screw	4	K048-52 with recovery of oil	6
IT	Indirect rotary kiln	—	Organics recovered or destroyed in afterburner	—
Chemical Waste Management	Indirect rotary kiln	5	Organics recovered	7
Roy F. Weston	Indirect screw — oil heated	7	Organics recovered	8, 9
ReTec	Indirect screw—molten salt heated	0.45	Organics recovered	10
AOSTRA Taciuk SoilTech (UMATAC/Canonie)	Direct rotary vessel	10	Organics recovered	11
TPS Technologies	Direct rotary kiln	23	Organics destroyed in afterburner	12
Site Reclamation Systems	Direct rotary kiln	—	Organics destroyed in afterburner	12

many organic compounds including high boiling compounds (PCBs) could be successfully separated from solids such as soil and sand. Since then, a process has been defined and scaled up to a 115 metric tons per day commercial unit. U.S. Patent No. 4,864,942 has been granted for the process.

The process can handle soils and dewatered solids such as pond sludge and filter cakes. Organic contaminants can range from high boiling, semi-volatile compounds such as PCBs to low boiling, volatile compounds such as RCRA regulated solvents [3, 4].

In the course of the development effort, treatment systems have been built at three distinct sizes, termed laboratory-scale, pilot-scale and commercial. Each of the three systems is discussed in this paper. The laboratory units are used for performing bench scale treatability studies. The pilot-scale system was used to confirm the design parameters and is now used as a demonstration unit. The first commercial unit is in shakedown testing and will be moved to a Superfund site in 1991.

FIGURE 1. Process flow diagram.

PROCESS DESCRIPTION

The process separates volatile or semi-volatile compounds from a solid matrix using thermal energy as the driving force. As shown in Figure 1, the process is fully continuous and is composed of two main elements, a dryer and a gas treatment system. The dryer heats the solids and volatilizes the water and organic contaminants. The gas treatment system condenses and collects the volatilized compounds, water and organics, and is the system's air pollution control (APC) system.

Feed material, which can be either a solid or a pumpable sludge, is fed into the dryer. For solids, a considerable effort has been expended on developing rugged and reliable feed hoppers and injectors which can handle widely varying feedstocks, including sandy, loamy and clay soils. The dryer is an externally fired rotary kiln, essentially a sealed rotating cylinder with the feed material tumbling inside and the heat source (propane burners) on the outside. Since the dryer is externally fired, the combustion products do not contact the waste material (feed) being processed. The use of an externally fired dryer has two distinct advantages. First, and most importantly, the combustion gases do not pass through the associated air pollution control devices. Propane is a readily available clean burning fuel. Air permits for vent stacks from propane combustors are easily obtained, usually without any required air pollution control (APC) devices. This allows the APC devices for the system to be one tenth to one hundredth of the size of that for an equivalent capacity incinerator. Also, the small amount of gas which has been in contact with the waste makes cleaning the vent stream to very high standards quite inexpensive. The second advantage of external firing is that it makes the system a separation process, not an incinerator, because no organic combustion occurs. It is usually much easier to permit a separation process than a waste incinerator.

The heated solids are discharged from the dryer as a powdered or granular dry material. For most applications, water will be mixed with the exiting solids to cool them and to prevent dusting. This water will normally be condensate from the gas treatment system.
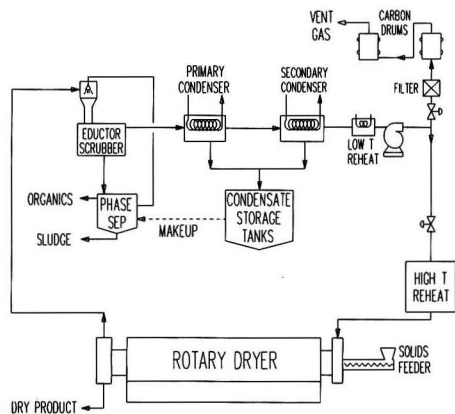
Table 2   Laboratory Test Results · SSM-I

Compound	Feed Conc (ppm)	Product Conc (ppm)	% Removal
VOLATILES			
Acetone	2,600	16.0	99.38
Total Xylenes	2,400	9.50	99.60
Ethylbenzene	1,600	5.20	99.68
Styrene	200	<0.005	>99.99
Tetrachloroethylene	150	0.094	99.94
Chlorobenzene	110	0.180	99.84
1,2 Dichloroethane	38	0.062	99.84
SEMI-VOLATILES			
Anthracene	4,650	12.0	99.74
Bis(2-Ethylhexyl)Phthalate	2,380	<0.33	>99.99
Pentachlorophenol	497	2.8	99.44

Table 3   Laboratory Test Results · Silt, Clay, Gravel

Compound	Feed Conc (ppm)	Product Conc (ppm)	% Removal
PCBs	805	17.2	97.9
Total Xylenes	18.8	<0.125	>99.3
1,2,4 Trichlorobenzene	24.8	<0.330	>98.7
Di-N-Butylphthalate	13.2	<0.330	>97.5
Pentachlorobenzene	11.6	<0.330	>97.1

The water and organic materials which are volatilized in the dryer are swept to the gas treatment system using an inert carrier gas (nitrogen). There, the gases are cooled, particulate material is removed and the water and organics are condensed. The carrier gas is then reheated and recirculated back to the dryer.

The carrier gas first passes through a liquid scrubber where entrained solid particles are removed and the gas stream is cooled to its saturation temperature. The water for this scrubber is continuously recirculated, with makeup water being supplied from previously condensed water. The scrubber also removes a portion of the volatilized organics. The recirculated scrubber water continuously passes through a phase separator, which collects any condensed light organic from the liquid surface and continuously discharges a bottom sludge containing solids, water and organics. The sludge is typically dewatered

using a filter press. The filtered liquid is returned to the scrubber supply. The dewatered solids are either returned to the feed stream or disposed of.

The scrubbed gas passes to a first heat exchanger where it is typically cooled to 5°C above ambient temperature. This heat exchanger will produce the bulk of the liquid condensate. The carrier gas then passes to a second heat exchanger where it is cooled to 4°C. The liquid condensates from both heat exchangers are mixed and allowed to gravity separate. Floating organics are removed for disposal. Any heavy organics (PCBs or chlorinated solvents) are removed from the bottom for disposal. The remaining condensed water is used to cool and dedust the treated solids exiting the dryer.

The 4°C carrier gas now contains some residual moisture and organics at levels equal to or less than their equilibrium saturation concentration at 4°C. The carrier gas is then recir-

Table 4   Laboratory Test Results · Non-PCB Soil, Sludges and Mixture

Run No.	Parameter	Concentration Feed	Concentration Product
DB0627	Total Solids (%)	94.1	100
Clay Soil	Ash (%)	92.6	99.8
	3,3'-Dichlorobenzidine (mg/kg)	1,716	<0.66
	Nitrobenzene (mg/kg)	42.9	<0.33
	Azobenzene (mg/kg)	3,000	4.9
	2-Chloroanaline (mg/kg)	779	ND
	Benzidine (mg/kg)	792	ND
DB0629	Total Solids (%)	73.1	100
Soil/Sludge	Ash (%)	71.6	99.7
	3,3'-Dichlorobenzidine (mg/kg)	700	<0.66
	Azobenzene (mg/kg)	44.6	ND
	Benzidine (mg/kg)	13.0	ND
DB0710	Total Solids (%)	47.0	100
Sludge	Ash (%)	44.7	100
	3,3'-Dichlorobenzidine (mg/kg)	503	<0.66
	Azobenzene (mg/kg)	16.8	ND
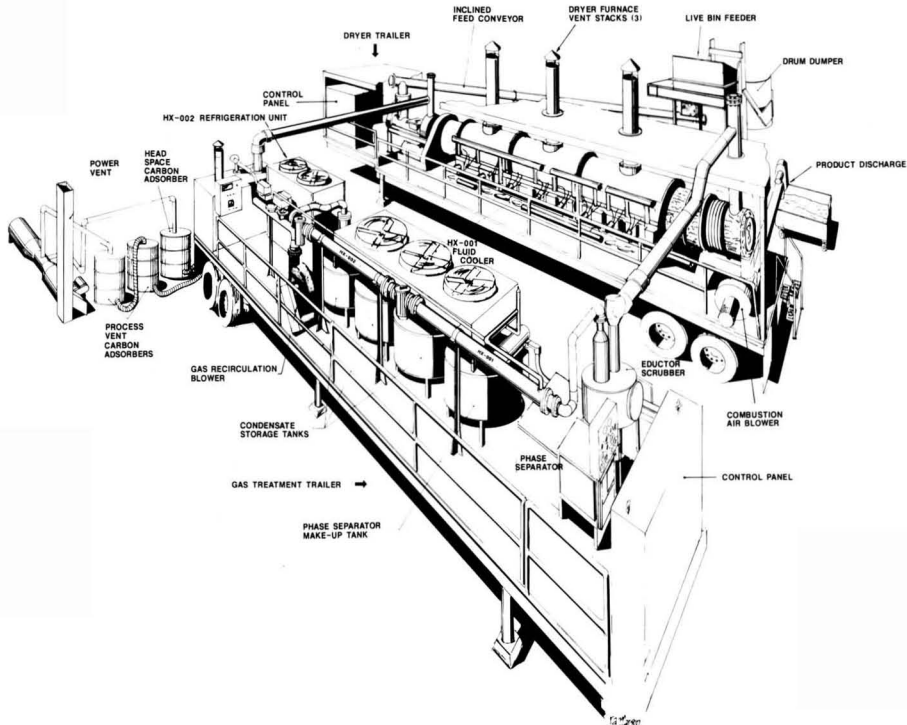
FIGURE 2. Artist's concept of pilot system.

culated through a blower. After the blower, 5 to 10% of the carrier gas is vented, and the remainder is heated to 200–400°C before returning it to the dryer.

The process vent gas stream passes through a particulate filter (typically a two micron filter) and then through a carbon adsorber, where at least 80% of the remaining organics will be removed. Actual practice has shown removal efficiencies by the carbon ranging from 89 to 98%. This gas is then vented to the atmosphere. A 90 metric tons per day system would release anywhere from 0.1 to 2.3 kg per day of VOCs which is considerably lower than most regulatory constraints.

LABORATORY TESTING PROGRAM

In January, 1988, operation of a laboratory system was initiated. This system typically processed one to two kg/hr of waste. It consisted of a 10 cm diameter, 122 cm long electrically heated tube furnace coupled to a small scale gas treatment system that closely simulates that for the pilot and full scale systems. Although it was considered laboratory scale equipment, it occupied a space of about 5 m by 7.5 m.

This unit was used for treatability studies and for screening materials for pilot testing and commercial operations. A total of 23 separate test runs was performed, with 19 being on actual RCRA and TSCA waste materials. The laboratory system was operated under a TSCA R&D permit and an Illinois authorization for RCRA treatability studies.

In September of 1989 the laboratory system was transferred to a subsidiary, Chem-Nuclear Systems Inc. (CNSI) in Barnwell, SC. CNSI has used the system to evaluate the applicability of the process for treatment of mixed (radioactive/hazardous) wastes [13]. A second laboratory system was constructed and became operational in June, 1990.

Table 2 presents the results on a simulated Superfund soil mixture prepared for EPA. This material was orginally referred to by EPA as the Synthetic Analytical Reference Matrix, or

SARM. It is now called Synthetic Soil Matrix, or SSM. SSM-1 had high organics concentration and low metals concentration. For both the volatile and semi-volatile organics, better than 99% removal was achieved.

Recently, lab tests were performed on two soil samples from potential remediation sites. The first was from a Superfund site with primarily PCB contamination, but also with some volatile organic contamination. The soil matrix consisted of silt, clay and gravel. Results are presented in Table 3. Of particular interest was the presence of Aroclor 1260, the highest boiling PCB. Total PCBs were reduced from 805 ppm to 17.2 ppm.

A more recent test was on samples of soil, pond sludge and mixtures thereof, all from the same site, which is a large remediation project estimated to have in excess of 500,000 metric tons of contaminated material. The organic contamination was a complex mixture of chlorinated semi-volatile organics, aromatics and organic solvents. A summary of the test results is presented in Table 4.

Treatment standards for this remediation have not yet been developed. If the treatment levels are set on a risk basis, it is very probable that the treated product would be acceptable.

PILOT TESTING PROGRAM

The pilot system is a mobile unit mounted on two semi trailers, one containing the dryer and another containing the gas treatment system. The pilot system has a nominal capacity of 4.5 metric tons per day for a feed material containing 30% moisture. Figure 2 is an artist's rendering of the pilot system.

The pilot system became operational in January, 1988. It was then tested on simulated contaminated soil feeds until July. During that time over forty tests were performed and in excess of 45 metric tons of material were processed. These tests proved the operability and reliability of the major pieces of equipment that were chosen for the system. They also established a large

Table 5 Pilot Operations · Surrogate Feed Materials

Compound	Feed Conc (ppb)	Product Conc (ppb)	% Removal
Methyl Ethyl Ketone	100,900	<100.0	>99.90
Tetrachloroethylene	91,000	15.6	99.98
Chlorobenzene	61,800	6.5	99.98
Xylene	56,400	2.8	99.99
1,4 Dichlorobenzene	78,400	1.4	99.99
1,2 Dichlorobenzene	537,000	74.1	99.99
Hexachlorobenzene	79,200	300.0	99.62

Table 6 Pilot Operations · Sandy Soil with PCBs (0727)

Compound	Feed Conc (ppb)	Product Conc (ppb)	% Removal
PCBs	1,480	8.7	99.4
1,2,4-Trichlorobenzene	2.9	ND	>99.9
Di-n-Butylphthalate	1.0	0.24	76.0
Bis(2-Ethylhexyl)Phthalate	9.1	0.18	98.0

body of data on the effectiveness of the separation process for various organic chemicals from a number of different soil matrices. These data are briefly summarized in Table 5. Also, material balance, heat transfer and effluent quality data were gathered and factored into the design of the full commercial scale system.

The pilot system was then disassembled and transported to the Department of Energy's Oak Ridge Gaseous Diffusion Plant in Tennessee where it was demonstrated on a mixed waste stream containing both RCRA-regulated organics and metals and DOE-regulated radioactive materials [14]. This test was successfully completed in late October, 1988, and the unit was then decontaminated and refurbished in preparation for its next phase of testing. Radiological material containment was very effective. All tests were run in a minimally controlled part of the facilities parking area, with no radiological problems.

After refurbishment, the unit was installed in early 1989 at Chemical Waste Management's Kettleman Hills facility in Central California for a rigorous series of tests on actual TSCA- and RCRA-regulated waste materials. Kettleman Hills is a fully permitted RCRA and TSCA treatment, storage and disposal facility. The pilot unit will be operated there at least through part of 1991 as a research project.

The system is operated under a variety of permits at Kettleman Hills. The most basic of these is an operating permit from Kings County, allowing an air emission source. CWM also has a variance from the California Department of Health Services to treat non-RCRA wastes such as California special wastes. The testing on PCB materials was conducted under a three month R&D permit from the EPA's TSCA branch, which expired October 4, 1989. A 90 day extension was granted starting November 1, 1989. CWM was recently granted a RCRA RD&D permit to allow testing on RCRA-regulated materials.

A total of ten PCB-containing soils was evaluated under the TSCA R&D permit. The last test was completed on January 26, 1990. Approximately 16 metric tons of material was processed.

The first PCB material test was conducted on July 27, 1989. The material was a sandy soil with some clay taken from a Superfund site. The site has formerly been used for solvent recycling and was primarily contaminated with PCBs, but also was known to have minor chlorinated solvent contamination. Table 6 is a summary of the performance data from this test run. During the test 2,250 kg of material were processed in ten hours. The system performed as expected, and small quantities of organic liquid were condensed, with PCB concentrations of up to 99,100 ppm. The resulting treated soil product samples had total PCB concentrations of 8.7–14.7 ppm, which were substantially below the site's treatment standard of 25 ppm. These results demonstrated at a relatively large scale that the process can separate PCBs from soil and produce a treated product with very low residual PCB concentration.

The second test was on a soil matrix of clay, silt and gravel. This soil was from the same site described previously as being tested in the laboratory unit (see Table 3). This was a Superfund site with primarily PCB contamination, but also having some solvent contamination. During this second test run 2,040 kg of material was processed. The results are presented in Table 7. The PCBs were reduced by over 99% to 19 ppm.

During pilot plant testing, the most persistent mechanical problem has been operation of the solids feed system. Soils with high sand concentrations presented few problems. However, soils with high clay content proved very difficult to convey at a constant rate, and sometimes at any rate. Over the last two years four different feed systems have been tried. Each of the first three were modified several times before progressing

Table 7 Pilot Operations · Clay, Silt & Gravel with PCBs (0810)

Parameter	Feed Conc	Product Conc	% Removal
Total Solids (%)	88.5	100	NA
TPH (mg/kg)	1,400	34	97.6
PCB (1254) (mg/kg)	2,800	19	99.3
1,2,4-Trichlorobenzene (mg/kg)	6.8	ND	>98.0
Di-n-Butylphthalate (mg/kg)	6.9	0.18	97.4
Bis(2-Ethylhexyl)Phthalate (mg/kg)	4.7	ND	>97.2
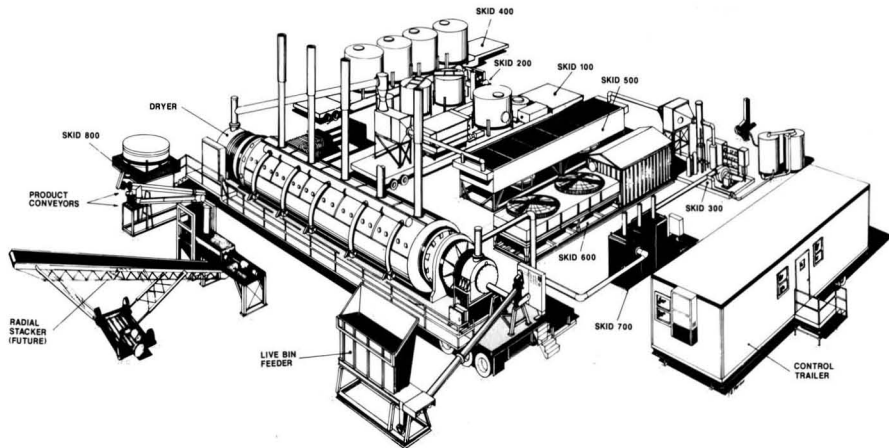
FIGURE 3. Artist's concept of full scale system.

to the next design. The current feed system has proven itself capable of metering and conveying anything from dry sand to damp clay that had to be picked out of an inverted drum.

SYSTEM DESCRIPTION

A full scale production system has been constructed for onsite cleanup of contaminated soil. The system is capable of treating 115 metric tons per day of contaminated soil with a moisture content of 20%. Like the pilot system, the full scale unit has a rotary dryer and a gas treatment system; however, they are much larger, requring the use of modular construction techniques. The system is fully transportable, consisting of three semi trailers, one control room trailer, eight equipment skids and various pieces of movable equipment. Figure 3 is an artist's rendering of the system. The area required for the equipment measures about 36 m by 36 m.

All of the equipment has been designed for over the road transport anywhere in the U.S. or Canada. The dryer is the largest of its kind that can be transported over the road. The components are mobilized to the project site and assembled using a relatively small crane. Approximately three to four weeks is required to completely install the equipment. Site preparation involves grading the site level and providing a firm base such as compacted gravel. Concrete footings are not usually required; however, concrete housekeeping pads may be. All skids or trailers that normally contain liquids have integral containment curbs for spill control.

The system requires three phase, 460 volt electric power, propane storage tanks and a liquid nitrogen storage tank. The electric motors are sized such that the system can be operated from a commercially available diesel generator if electric power is not available at the site.

Operation involves screening the feed material to remove oversize material such as rocks, wood, etc. The material handling system limitation is six cm size materials. Screened material is then placed into the system's feed hopper directly from a front end loader. The feed is then conveyed into the dryer, where the organics are thermally separated from the solids. The hot solids are conveyed from the dryer to the system's product cooler, where previously condensed water is added to cool and dedust the product. Treated product is conveyed from the system, stockpiled and is then typically returned to the site as backfill after confirmatory analysis shows that the treatment standard has been met.

The gas treatment system employs an eductor scrubber for

particulate solids removal, followed by two condensers, the first air cooled and the second refrigerated. This process design is identical to the pilot system. The condensed organic liquids are phase separated in an inclined plate separator and stored in holding tanks for disposal. The scrubber's phase separator has both sludge and scum removal capability. Sludge and scum are accumulated in tanks and then filtered with a skid mounted filter press. Filtrate is recycled to the system, phase separated organics are stored for disposal and filter cake is either reprocessed as feed to the dryer or disposed of.

The system is monitored from the control trailer, which is a heated and air conditioned portable office trailer. All aspects of system operation can be monitored from the control trailer, and all essential process control parameters can be adjusted.

The system has been operated on non-contaminated feed materials at rates of over 110 metric tons per day. The commercial unit will be transported to North Dartmouth, MA during 1991 and will be used to remove PCBs from approximately 32,000 metric tons of soil at the Resolve site. The condensed oil will then be dechlorinated.

CONCLUSIONS

The process has been demonstrated to be an effective method for removing organic contaminants from soils. Concentrations of even very high boiling compounds such as PCBs can be reduced to low levels in the treated soil. The laboratory scale system has proven to be ideal for feasibility testing on relatively small samples. The pilot scale system requires at least two metric tons of sample and produces data that can be used to accurately estimate a remediation. The first commercial system will become operational during 1991 on a Superfund site.

Treatment prices are highly dependent on many variables, but will typically range from $165 to $275 per metric ton of feed processed.

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Advanced Non-Catalytic Post Combustion NOx Control

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The effectiveness of combustion modifications, including staged combustion and reburning, for the control of nitrogen oxide emissions from coal or oil fired combustors is most often limited by problems due to carbon burnout or flame impingement. This paper presents new data on the use of selective reducing agents, such as ammonium sulfate, suggesting that a hybrid control scheme is possible which uses combustion modification to provide those conditions which optimize the selective reduction process. Very low emission levels appear possible that can presently only be achieved by catalytic reduction.

INTRODUCTION

Combustion of fossil fuels, especially coals and heavy oils, produces significant amount of NOx which ultimately participate in the formation of smog and acid rain. Combustion modification concepts including staged combustion [1] and reburning [2] have been effective in achieving up to 60 percent NOx reductions. Downstream injection of selective reducing agents, particularly ammonia [3] and urea [4], can produce significant additional reductions. However, the temperature window over which these reagents are effective is relatively narrow.

This paper summarizes the results of a study which was undertaken to investigate the possibility of positive synergism between the injection of various selective reducing agents, such as ammonia, and more conventional combustion modifications. The experimental studies were conducted in a 25 kW$_t$ refractory lined tunnel furnace. The work focused on the importance of reaction temperature, local stoichiometric ratio, and the composition of the selective reducing agent. Cyanuric acid [5], urea, ammonium sulfate, and ammonia gas were considered as selective reducing agents. Fuel rich and fuel lean conditions were included in a temperature range of 600 to 1300°C. These studies were subsequently supported with testing in a 3.0 MW$_t$ pilot scale facility and with kinetic modeling.

EXPERIMENTAL

The bench scale experiments were conducted in a 15.2 centimeter diameter by 2.4 meter long refractory lined tunnel furnace [2]. All data reported here are for natural gas firing in a 15 kW$_t$ premixed burner. The oxidant was air and ammonia was added to the natural gas to provide the desired level of post-flame NO. The NO values, along with all other concentrations, are reported on a dry basis, corrected for dilution to 0.0 percent O_2. The temperature was declining at a rate of 225°C/s throughout the region of interest in this study. When the furnace was operated to simulate stage combustion, the gases from the first stage, normally fuel rich, were mixed with burnout air via a radial injector positioned on the furnace axis. The temperatures reported for the staging location are those of the furnace gas immediately after the staging air has been added and mixed. When the furnace was operated to simulate reburning, the reburning fuels were injected with a 90° injector located at the centerline of the furnace. This injector allowed the reburning fuel, diluted/transported with argon, to flow radially outward through four 0.5 cm holes and mix rapidly with the oncoming primary effluent. Burnout air was also injected radially.

The 3.0 MW$_t$, down-fired tower furnace [2] used in the pilot-scale investigations was refractory-lined and water-jacketed with inside dimensions of $1.2 \times 1.2 \times 8.0$ m. The four main diffusion burners each consisted of an inner pipe for axial primary fuel injection and an outer pipe, equipped with swirl vanes, for the main combustion air. The four burner array produced relatively uniform velocity and composition profiles at the primary zone exit. The furnace contained seven rows of ports for reburning fuel and burnout air injection. The temperature profile was manipulated by insertion of cooling panels, positioned against the furnace walls. The reburning fuel and burnout air injectors were designed to maintain jet mixing

FIGURE 1. Influence of injection temperature and reducing agent composition.

symbols and solid lines represent these data, and for these tests the peak temperature refers to the temperature at which the final burnout air was added. The selective reducing agent was added into the fuel rich zone at 900°C. Other compounds such as ammonium sulfate, which are significantly less expensive and potentially less toxic, can produce even larger reductions than those measured with cyanuric acid.

Kinetic modeling suggests that the rich zone acts primarily as a source of CO. At the rich-lean transition the CO is oxidized and excess OH is produced by the usual chain branching reactions:

$$CO + OH \rightarrow CO_2 + H$$

$$H + O_2 \rightarrow OH + O$$

$$O + H_2O \rightarrow OH + OH$$
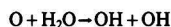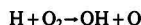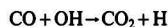
For low initial CO concentration the excess radicals are consumed by:

$$NH_3 + OH \rightarrow NH_2 + H_2O$$
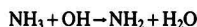
The NH_2 is then available for reaction with NO to eventually yield N_2.

The above results suggest that the key parameters for the enhancement of burnout zone chemistry in staged combustion or reburning are:
- Reaction temperature (850°C),
- CO level (0.5% or less), and
- NH_3 species.

Advanced Reburning

Apparently the conventional reburning process does not provide the required environment. An advanced reburning process [7], which combine reburning with selective NO_x reduction (SNR) via ammonium sulfate injection, was designed and tested. Figure 2 shows two hybrid schemes with 20 percent and 10 percent gas reburning, respectively. With 20 percent reburning ($SR_2 = 0.9$), the burnout air was divided into two streams to yield an SR_3 of 0.99 and an SR_t of 1.15. With 10 percent reburning, the reburning zone stoichiometry (SR_2) was 0.99 and the burnout air stoichiometry (SR_t) was 1.15. In both cases, an aqueous solution of ammonium sulfate was atomized with the final burnout air and injected at 850°C at an N to NO molar ratio of 1.5. Figure 3 presents the results obtained with natural gas as the primary fuel. The natural gas was doped with NO to provide two levels of primary NO_x, 600 and 240 ppm (dry, 0 percent O_2). Twenty and ten percent reburning

similarity between the pilot-scale furnace and a full scale boiler based on empirical correlations for entrainment rate and jet penetration.

Exhaust gas samples were withdrawn through a stainless steel, water-jacketed probe and analyzed for NO_x (chemiluminescence), O_2 (paramagnetic), CO/CO_2 (NDIR), and SO_2 (NDUV). A water-jacketed probe with an internal water quench spray near the front end was used for extracting in-flame samples. Gas phase HCN and NH_3 species were collected in a gas washing unit and subsequently analyzed for CN and dissolved ammonia using specific ion electrodes. Gas temperatures were characterized with a suction pyrometer.

RESULTS

Original Concept: Staged Air Addition

Figure 1 summarizes a series of experiments [6] which were conducted in the tunnel furnace with an initial NO concentration of 240 ppm and a $-N$ to NO ratio of 1.5. The solid symbols and dotted lines show results for cyanuric acid or ammonium sulfate injection under classical "De-NO_x" conditions with 25 percent excess air and indicate an optimum reaction temperature of approximately 1000°C as has been reported previously [3]. Somewhat surprisingly, however, significantly larger reductions can be achieved over a broader temperature range if the selective reducing agent is added under slightly fuel rich conditions (in this case $SR_1 = 0.99$), and the final burnout air is added subsequently downstream. The open

FIGURE 2. Advanced reburning configurations.
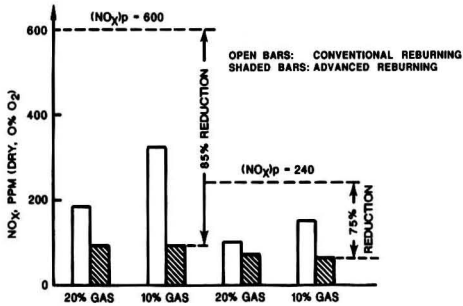
FIGURE 3. Advanced reburning-bench scale results.

FIGURE 4. Pilot scale results with Indiana Coal.

were applied separately in both cases. These data indicate that a hybrid process which utilizes 10 percent reburning fuel can achieve similar overall efficiency to a process using 20 percent reburning. It is apparent that there exists a tradeoff between natural gas premiums and the cost of ammonium sulfate.

Pilot Scale Verification

A series of experiments were first carried out with natural gas as the primary fuel to define the optimum stoichiometry distribution for the advanced reburning process at pilot scale. Measurements of CO and O_2 concentrations were conducted at the ammonium sulfate injection location, approximately at 900°C. Results obtained indicated that in order to have an optimum CO level between 1500 and 2000 ppm (corresponding to approximately 0.7 percent O_2) at the reagent injection location, it was necessary to increase the local stoichiometry from 0.99, as defined in the bench scale studies, to 1.03 to account for the finite rate mixing and higher CO concentrations in the

pilot scale furnace. Experiments were subsequently carried out with an Indiana coal as the primary fuel. The Indiana coal produced an uncontrolled NO_x emission of 800 ppm (dry, 0 percent O_2) at 15 percent excess air. The primary NO_x at $SR_1 = 1.13$ was 680 ppm. Figure 4 presents the results and indicate that as seen in the bench scale studies, both advanced concepts were equally effective in NO_x reductions. Similar results were also obtained with a Utah coal as the primary fuel (primary $NO_x = 850$ ppm, Figure 5).

Figure 5 summarizes all of the pilot scale results and compares with the bench scale data. The ratios of $(NO_x)_{EX}$ to $(NO_x)_p$ are presented as a function of $(NO_x)_p$ concentrations. It can

OPEN SYMBOLS = 100 X 10³ BTU/HR
SOLID SYMBOLS = 5 X 10⁶ BTU/HR
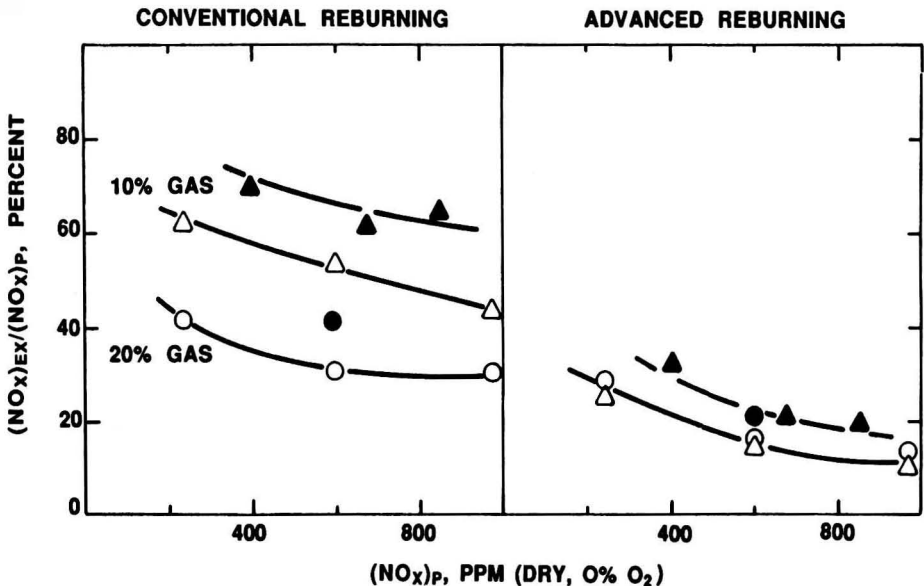
FIGURE 5. Scale effect.

Table 1 By-Product Emissions with Indiana Coal

Condition	NH3 (ppm)	SO2 (ppm)	SO3 (ppm)
Uncontrolled	0	1380	10
10% Gas	<2	1500	13
20% Gas	<2	1400	9

be seen that for both conventional reburning and advanced reburning, the process efficiency depends on the $(NO_x)_p$ level, higher efficiency at higher $(NO_x)_p$. Also, substantial scale effects were observed with conventional reburning. However, with advanced reburning the effect of scale was much less significant. Approximately 7 percent loss in process efficiency was observed when scaled up from 100×10^3 Btu/hr to 5×10^6 Btu/hr at a factor of 50 times.

By-Product Emissions

The injection of ammonium sulfate into the furnace has a potential of producing unwanted emissions such as NH_3 and So_2/So_3. A series of exhaust measurements were made to evaluate the slip of ammonia using selective ion electrode and the emission of SO_2 and SO_3 via controlled condensation. Table 1 summarizes measurements made during the Indiana coal tests. Exhaust NH_3 concentrations were negligible in all cases, including those obtained with Utah coal and natural gas as the primary fuel. Higher SO_2 emissions were obtained with 10 percent gas reburning. However, the uncontrolled SO_2 level was maintained with 20 percent gas reburning due to dilution. No increase in SO_3 emissions was observed for both cases, suggesting favorable conversion of the sulfate to SO_2.

Thus, there exists a control strategy to prevent an increase in SO_2 emissions due to the injection of ammonium sulfate. For the application of advanced reburning to high sulfur coals, 10 percent gas reburning is recommended, whereas for low coal applications, the 20 percent gas reburning concept is preferred.

CONCLUSIONS

In summary, these results suggest that selective reducing agents can be combined with combustion modification techniques to provide NO_x reductions that are larger than those that are possible by applying the technologies simultaneously but separately. By using the stoichiometry control associated with reburning to produce a slightly fuel rich region for selective reducing agent injection, reductions can be achieved at relatively low temperatures without the use of stainless steel or other catalysts. In principle, this technology could have broad application to fossil fuel fired furnaces and boilers, stationary gas turbines, and internal combustion engines.

ACKNOWLEDGMENTS

DISCLAIMER

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The Direct Sulfur Recovery Process

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The Research Triangle Institute under contract to the U.S. Department of Energy, Morgantown Energy Technology Center, is developing the Direct Sulfur Recovery Process (DSRP) for converting either reduced or oxidized sulfur gases directly to elemental sulfur. Laboratory tests were conducted to evaluate the effects of stoichiometry, pressure, temperature, space velocity and steam content. Pressure was found to be the most important variable. Increasing pressure from 1.5 atm to 20 atm quadrupled the sulfur recovery at equivalent space velocity. Sulfur recoveries from dilute SO_2 streams were greater than 96% in tests simulating the first stage of reaction. In the first stage of reaction, SO_2 is directly reduced to elemental sulfur by coal gas or other reducing gases at high temperature and high pressure. Under second-stage reaction conditions, recoveries ranged from 80 to 98% depending on operating conditions. Combined with a first-stage conversion of 96%, this translates into overall conversions of 99.2 to 99.9%. Preliminary economic comparisons with conventional processes that could be used for treating dilute SO_2 tail gases showed a decisive cost advantage for the new catalytic process. The effectiveness of the high-pressure, high-temperature DSRP on H_2S containing gases has also been demonstrated. Direct conversions of H_2S to elemental sulfur ranged to 98% in a single stage of reaction using near stoichiometric amounts of air or oxygen. Bench-scale development is ongoing to investigate a variety of reactor types and configurations.

INTRODUCTION

Currently in the United States, elemental sulfur in large measure is recovered by steam injection into underground deposits using the thermally inefficient Frasch process. Concern is growing that the deposits may dwindle in capacity and that Frasch production may end by the year 2000 [1]. Natural gas and petroleum processing is another large source. Dwindling production of natural gas and petroleum in the U.S. will further limit the supply of sulfur. Sulfur is mostly used to produce

sulfuric acid, the largest single chemical produced in the U.S. The U.S. consumed over 11 million long tons of sulfur in 1988 [2]. Elemental sulfur production also offers an alternative to flue gas treatment processes that produce large volumes of throwaway waste that must be disposed of in an environmentally safe manner. Furthermore, international environmental concerns have engendered the commercialization of a number of modified Claus processes enhanced with tailgas treatment processes [3].
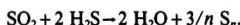
The U.S. Department of Energy's (DOE) Morgantown Energy Technology Center (METC) is developing a hot, coal gas desulfurization concept based on a regenerable zinc ferrite sorbent [4]. The potential benefit of hot-gas cleanup is most significant when the hot clean gas fuels a gas turbine in an integrated gasification/combined cycle (IGCC) system. In the zinc ferrite process, hydrogen sulfide reacts with zinc ferrite, which is regenerated by a dilute air stream. This produces a hot regeneration off-gas containing 1 to 3% SO_2 which must be disposed of in an environmentally acceptable manner. The DOE/METC initiated a number of studies addressing the issue of disposal.

The Ralph M. Parsons Company, under contract to DOE, has evaluated the technical and economic feasibility of candidate processes that can recover sulfur from hot regeneration off-gas [5]. Four preferred process schemes based largely on concentration using Wellman-Lord scrubber technology were selected for in-depth economic evaluation. Gilbert/Commonwealth [6] evaluated a number of other options including conventional scrubber technology that results in a throwaway calcium sulfate product and even in-bed desulfurization where lime is injected into the bed of gasifying coal. Arthur D. Little Company, under contract to DOE, demonstrated that selected conventional flue gas desulfurization technology could be applied [7]. General Electric Company, under contract to DOE, is currently studying moving beds of mixed metal oxides for coal gas desulfurization followed by regeneration which results in a concentrated tailgas containing up to 13% SO_2. The concentrated tailgas may be used to produce sulfuric acid [8]. Alternatively, Research Triangle Institute (RTI) investigated several process concepts for the recovery of elemental sulfur from SO_2 containing off-gas [9]. The work at RTI resulted in the discovery of the Direct Sulfur Recovery Process (DSRP) which may be applied to sulfur-containing tailgases and other process streams.

PROCESS PRINCIPLES

The DSRP is capable of converting over 90% of the sulfur in gas streams containing reduced or oxidized gaseous sulfur compounds to elemental sulfur in a single-stage, continuous process. No preconcentration, oxidation, or reduction is necessary. If additional sulfur recovery is necessary, the inlet gas composition to the first reactor is controlled to produce Claus stoichiometry at the inlet of a second stage. Conversion of hydrogen sulfide and carbonyl sulfide to elemental sulfur is also possible, confirming the versatile nature of the DSRP. However, the work has focused largely on conversion of SO_2 to elemental sulfur.

The gas containing SO_2 is reacted over a catalyst with a quantity of reducing gas which simply may be a slipstream of available coal gas. The chemistry of the process invariably involves multiple intermediary reactions at or near the surface of the catalyst. Simple examples of the overall reactions are:

$$2 H_2 + SO_2 \rightarrow 2 H_2O + 1/n \ S_n$$

$$2 CO + SO_2 \rightarrow 2 CO_2 + 1/n \ S_n$$

$$SO_2 + 3 H_2 \rightarrow H_2S + 2 H_2O$$

$$SO_2 + 2 H_2S \rightarrow 2 H_2O + 3/n \ S_n.$$
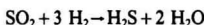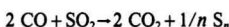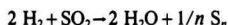
The first two reactions are rapid and not thermodynamically limited while the last reaction is the modified Claus reaction which is thermodynamically limited. Thermodynamic calculations predict 50 to 60% completion for the last reaction under typical DSRP operating conditions. Experimentally, recoveries of sulfur from dilute SO_2 streams were at times greater than 96% in tests simulating the first stage of reaction. Therefore, kinetic control by the first two reactions may be the overriding
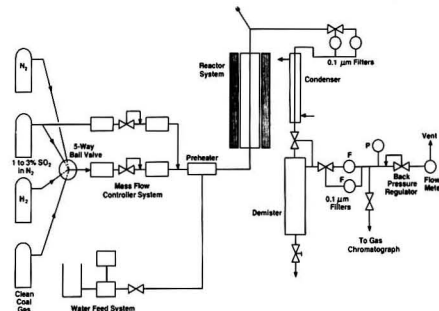
FIGURE 1. High-pressure fixed-bed reactor system

mechanism, at least during the initial stages of reaction. However, uncertainty in the form of sulfur, as noted by "n" in the equations above, and the thermodynamic database at high temperature and pressure conditions cloud the issue. Other researchers reported similar discrepancies between experimental data and thermodynamic predictions [10, 11, 12]. The thermodynamic database may need to be revised for the various sulfur forms at high-temperature and high-pressure (HTHP) conditions.

EXPERIMENTAL APPARATUS

Tests simulating the two DSRP stages were performed using the fixed-bed reactor system shown in Figure 1. The system at RTI consists of a 2.54-cm O.D., 2.21-cm I.D., Alon processed 316 stainless steel reactor, a gas feed system, and filter/condenser for the removal of elemental sulfur and water. Premixed or high-purity gases flow from pressure-regulated gas bottles, controlled by mass flow controllers. A high pressure, positive displacement pump injects water into the gases before an electric heater prior to entering the bottom of the reactor. The reactor holds either 25 or 50 cubic centimeters (cc) of catalyst in a fixed bed. After exiting the reactor, the gas is cooled to 435 K to condense sulfur on the filter. Water is removed in a condenser and then the dry gas flows through a back pressure regulator which controls the bed pressure. A sample of gas is continuously withdrawn before the back pressure valve. The gas is analyzed for H_2S and SO_2 by gas chromatography and a continuous SO_2 analyzer. Occasionally sulfur collected was weighed to close the mass balance around sulfur.

EXPERIMENTAL RESULTS

Tests were conducted to evaluate the effects of stoichiometry, pressure, temperature, space velocity, and steam content on sulfur recovery. Temperatures from about 665 K to 975 K were investigated for the first reaction stage. Lower temperatures down to 525 K were investigated for simulated second stage reactions after elemental sulfur removal in an intercooler between stages. Space velocities ranging up to 20,000 standard

Table 1 Variable inlet gas composition

Component	Stage I % by Volume	Stage II % by Volume
SO_2	0.85–1.9	0.5–0.6
H_2O	1.0–35.0	0–34
H_2	0.65–1.6	0
CO	0.85–2.1	0
CO_2	0.25–0.6	0.5–1.0
N_2	Balance	Balance
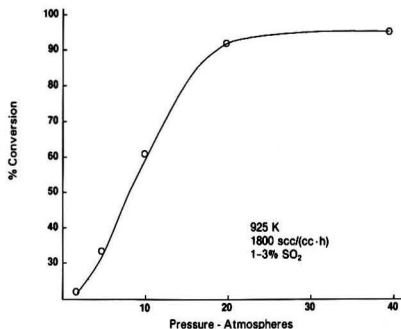
FIGURE 2. Effect of pressure on the DSRP—Stage I

FIGURE 4. Effect of temperature on the DSRP—Stage I

cubic centimeter per cubic centimeter per hour (scc/(cc·h)) were evaluated. Pressure ranged from essentially atmospheric to 20 atm and even to 40 atm at times. The work focused on the reduction of SO_2 to elemental sulfur in simulated coal gas; however, a number of test runs demonstrated the oxidation of H_2S with oxygen directly to elemental sulfur. A large database was generated dealing with the conversion of SO_2 to elemental sulfur over a wide range of conditions. Inlet gas compositions also varied widely as indicated in Table 1. The experimental results from Stage I simulations are summarized in Figures 2 through 6. Results from Stage II simulations are given in Figure 7. The percent conversion in the figures refers to the input gaseous sulfur converted to elemental sulfur. Figure 8 presents conversion of H_2S to elemental sulfur in a single stage over a range of pressures and temperatures.

In the first stage of reaction, the greatest effect was observed when pressure was increased, as shown in Figure 2, at a near constant temperature of 925 K. Beginning at slightly above atmospheric pressure, conversion to elemental sulfur amounted to about 20% which quickly rose to near 60% at 10 atm and then to over 90% near 20 atm pressure. Doubling the pressure to 40 atm increased the conversion to 95% in these early test runs. These results are surprising since thermodynamic calculations predict decreased conversion rates as pressure increases. These results were also obtained at a relatively high hourly gas space velocity near 1800 scc/(cc·h) in comparison to commercial Claus practice near 1000 scc/(cc·h). The higher pressure apparently permits higher space velocities and therefore smaller size reactors, or higher throughput with a fixed size of reactor. Space velocities even higher than 1800 scc/(cc·h) can be used in the DSRP, as evidenced by the results presented in Figure 3.

Stage-I data presented in the upper band of Figure 3 was obtained at a constant 20 atm pressure at temperatures from 825 K to 925 K. Up to the maximum space velocity shown at 5000 scc/(cc·h), conversion was impacted to a small degree, essentially remaining above 90% at the extreme flow rate. Space velocities ranging from 1800 scc/(cc·h) to 5000 scc/(cc·h) resulted in conversions varying between 90 and 95% near 825 K. The variation was less pronounced at the higher temperatures near 925 K, remaining closer to 95%. In contrast, the detrimental impact of space velocity on conversion at the lowest pressure tested, near 1.5 atm was dramatic.

The lower line in Figure 3 illustrates the impact on Stage I simulations. A variation in space velocity from 400 scc/(cc·h) to 1800 scc/(cc·h) cuts the conversion in half, i.e., from about 46% to near 20% at 1.5 atm. As a result, the slope of the lower line is much steeper than the upper band obtained at 20 atm pressure. Another comparison of the data presented in Figure 3 is useful. We can compare the results at varying pressure at a fixed space velocity of 1800 scc/(cc·h) and temperature of 925 K, i.e., point A at 1.5 atmospheres to point B at 20 atm. At the lower pressure, the conversion is near 20%, while at the higher pressure, the conversion is well over 90%. This confirms that pressure plays an important role in the DSRP.

Somewhat analogous to the effect of pressure is the effect of temperature on Stage I reactions, but to a lesser degree, as shown in Figure 4. At 715 K and above, conversion to elemental

FIGURE 3. Effect of space velocity and pressure on the DSRP—Stage I
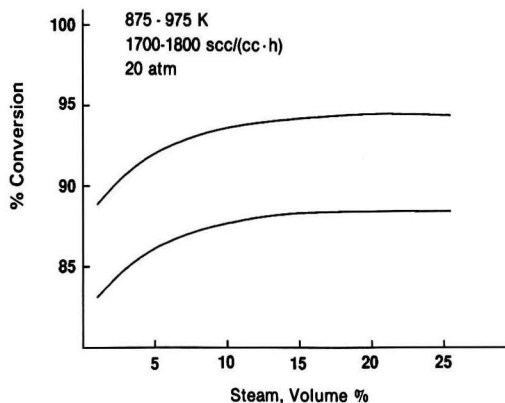
FIGURE 5. Effect of steam content on the DSRP
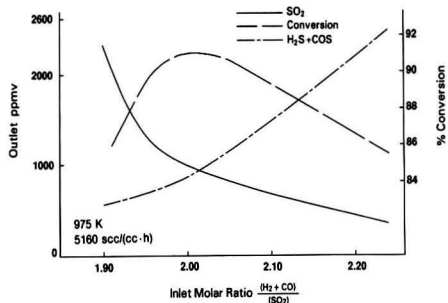
FIGURE 6. Effect of stoichiometry on the DSRP

DSRP for H$_2$S Containing Gas

$$2 H_2S + O_2 \rightarrow 2/n \; S_n + 2 H_2O$$

FIGURE 8. Direct single-stage conversion of H$_2$S to elemental sulfur

sulfur remains well above 90% and is essentially unaffected by any increase in temperature. These results obtained at a constant pressure of 40 atm are significant because the insensitivity of both conversion rates and catalyst to temperature rise is demonstrated. The catalyst has yet to show any signs of thermal degradation over hundreds of hours of testing including repetitive testing of a single catalyst material. The possible effects of thermal degradation may become more evident as the DSRP is scaled up in larger adiabatic reactors.

The effect of steam content of the gas on conversion of SO$_2$ to elemental sulfur in Stage I was evaluated. The Claus equilibrium is limited by the water content of the gas, which must be removed in the intercooling step between stages. However, this disadvantage for the Claus is not experienced with the DSRP Stage I at high temperature and pressure. Figure 5 shows results at 20 atm pressure and temperatures varying between about 875 K and 975 K. Steam content in the inlet gas ranged from about 1 to 25%, producing virtually no impact on the conversion rate above 5% steam. The effect below 5% may be questionable since data from some early runs are included which may not have been at optimal conditions. The insensitivity to steam indicates that the conversion at high temperature and high pressure is not limited by the Claus equilibrium. As the overall sulfur content in the gas drops to the ppm level, and H$_2$S and SO$_2$ levels become comparable, another equilibrium may be established which is not affected by steam content at high temperature and pressure. The data support the kinetic control by the direct reduction reactions discussed earlier. In contrast, the equilibrium products and conversion rates are dependent on stoichiometry.

Figure 6 presents the concentration of SO$_2$ and reduced sulfur compounds, COS plus H$_2$S, found in the outlet of Stage I as the molar ratio of reducing gases was varied. The molar
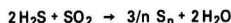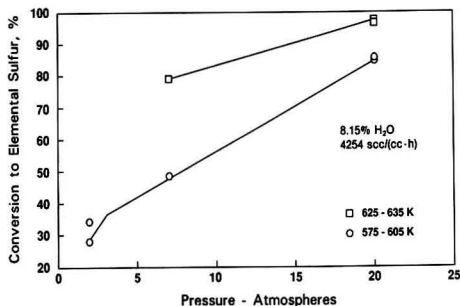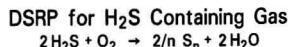
ratio was varied closely about the stoichiometric ratio of 2 moles of reducing gas, either as H$_2$ or CO, to one mole of SO$_2$ in the inlet. As the reducing content in the gas increases, the residual content of SO$_2$ in the gas decreases and the reduced compounds of sulfur increase. The data demonstrate that the components in the outlet can be controlled in preparation for a second stage of reaction. It is also known in Figure 6 that sulfur conversion is optimized as the stoichiometric ratio of 2.0 is approached, demonstrating the importance of controlling molar ratios at the inlet of the DSRP. The data also suggest that H$_2$S can be efficiently converted to elemental sulfur.

In addition to the parametric testing of the first stage of reaction, tests to evaluate the conversion rates in the second stage of reaction were also conducted. Figure 7 presents the results using two different catalysts at a constant pressure of 20 atm. To simulate the second stage of reaction, gas mixtures were prepared containing 2 moles of H$_2$S for each mole of SO$_2$. The mixture is readily produced by controlling stoichiometry at the inlet to the first stage of reaction as indicated in Figure 6. The Claus reaction takes place since H$_2$S is the only available reducing agent in these tests:

$$SO_2 + 2 \; H_2S \rightarrow 2 \; H_2O + 3/n \; S_n.$$
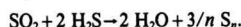
The conversions obtained using catalyst A were much higher, around 95%, than those with catalyst B which were no higher than 80% and decreased as the temperature increased. Conversions with catalyst A were essentially constant over the entire temperature range investigated. Any differences due to the variation in space velocity noted in the figure would be expected to be small.

As noted earlier in the discussion of data presented in Figure 6, H$_2$S in a gas stream might also be efficiently converted to elemental sulfur. Figure 8 presents the conversions of H$_2$S to elemental sulfur directly with dilute oxygen, over a range of pressure and two ranges of temperature. No precombustion, as practiced in the modified Claus process, was necessary. At the inlet of the reactor, the gas contained 6.46% H$_2$S, 3.23% O$_2$ and 8.14% H$_2$O with a balance of N$_2$. At the upper temperature range shown in the figure, near 635 K, the conversion of H$_2$S to elemental sulfur at 20 atm was above 98%. The conversion decreased as either the pressure and/or the temperature was lowered. The space velocity of 4250 scc/(cc.hr) is attractive in comparison to industrial practice of the Claus process. The data encourages further development of the DSRP for sulfide-laden gas streams found in oil, natural gas, and other refineries.

$$2 H_2S + SO_2 \rightarrow 3/n \; S_n + 2 H_2O$$

FIGURE 7. Stage II simulation tests
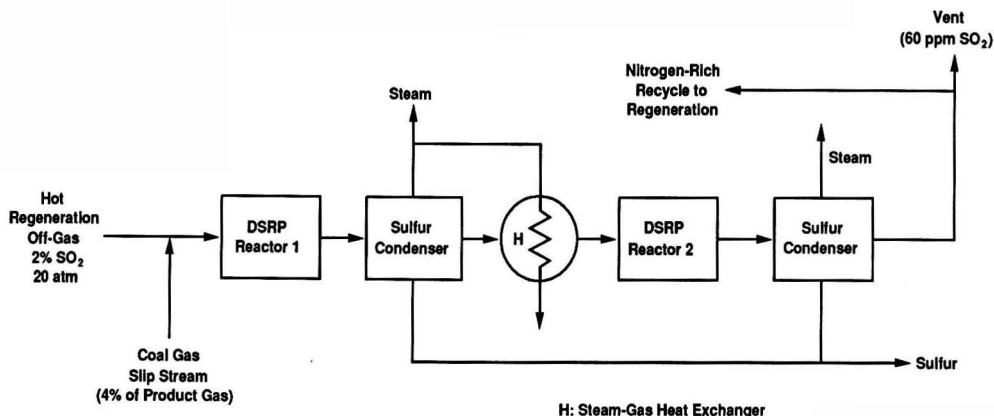
FIGURE 9. Conceptual design for DSRP in an IGCC power system

PRELIMINARY ECONOMIC ANALYSIS

A conceptual design was prepared for a DSRP plant to operate on a 100 MWe IGCC plant firing a high sulfur, Illinois coal. A schematic of the conceptual design of the DSRP is presented in Figure 9. Two stages of reaction are designed to recover better than 99.5% of the SO_2 from the zinc ferrite regeneration tailgas as elemental sulfur. The two sulfur condensers would run above the dewpoint of water to condense sulfur but not steam since the DSRP is insensitive to steam. After the second condenser the treated gas would contain about 60 ppmv of SO_2 which could be partially vented and recycled back to the zinc ferrite regenerator. Although the DSRP is shown as separate boxes in the figure, all process steps can conceivably be incorporated within a single pressure vessel or even integrated with the overall desulfurization process. Since recycle back to the regenerator or gasifier is possible, a 95% recovery rate in a single stage may be sufficient to meet environmental standards in certain cases. This could result in additional savings. In any event, the preliminary capital and operating costs developed for the DSRP appear to be a fraction of costs for conventional processes that might be used to treat the regeneration gas from hot coal gas desulfurization. Since the economic analysis was based on comparative factored costs, they need to be confirmed prior to reporting any further results.

CONCLUSIONS

Experimental results indicate that the DSRP can convert either SO_2 or H_2S directly to elemental sulfur at high conversions above 95%. Pressure has the most significant effects in terms of increased conversion to elemental sulfu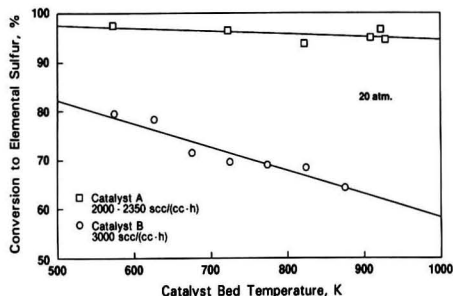r and increased throughput. Gas hourly space velocities near 5000 scc/(cc·h) increase the throughput in comparison to the Claus and other processes. Above a threshold temperature and depending on pressure, the conversions in Stage I remain above 90% with little impact caused by further increases in temperature. Stage II can operate at temperatures of 525 K or less to reduce reheat requirements between stages.

The DSRP is insensitive to the steam content of the gas which distinguishes it from other processes that rely on modified Claus equilibrium reactions. Gas streams containing concentrations of sulfur compound as low as a few tenths of a percent can be treated using the DSRP to efficiently recover elemental sulfur.

The conversion to elemental sulfur can be optimized by controlling the stoichiometric balance of gaseous components at the inlet of the Stage I reactor. No additional reactants are required for the Stage II reactor. Further work must be done at larger scale to confirm the promising laboratory results and economics of the DSRP.

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An At-Source Treatment for Organomercury-Containing Hazardous Liquid Waste

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An at-source treatment has been developed for the removal of mercury from a spent fermentation waste to render it non-hazardous. The organomercury-containing fermentation wastewater is initially treated with aluminum metal powder at pH 11.5 and ambient temperature to reduce the sulfur-hydrogen bond to form mercury cations and organomercury fragments. Subsequent treatment with sodium borohydride reduces the mercury cations and organomercury fragments to elemental mercury. Ultrafiltration is then used to effectively remove the colloidal metallic mercury. Final polishing with granular activated carbon yields an effluent containing less than 10 μg/l mercury. The colloidal mercury present in the UF retentate as well as that bound to the granular activated carbon is amenable to reclamation and subsequent reuse. The at-source treatment technology developed has been found to be capable of achieving a consistently high removal efficiency of 99.99%.

INTRODUCTION

The specific example discussed in this paper deals with the development of an at-source treatment technology for the removal and recovery of mercury from a spent fermentation waste. An organomercury compound (Thimerosal, Figure 1) is used as a slow kill biocide in one fermentation process. The Company's waste minimization policy mandated a thorough evaluation of various at-source treatment technologies to render the waste non-hazardous. It has been shown that it is possible to reduce the mercury concentration in the waste to below 10 μg/l from 56 mg/l by sodium borohydride reduction followed by ultrafiltration of the colloidal mercury metal followed by Granular Activated Carbon (GAC) polishing. Reclamation of the metallic mercury for recovery and non-process reuse was also found to be viable. The proposed process for the at-source reduction and removal of mercury, an environmentally sound waste minimization approach, is described in detail.

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REVIEW OF PROMISING TECHNOLOGIES

Three promising technologies were evaluated prior to the selection of metal hydride reduction as the method of choice. These were metal hydride reduction, free radical oxidation, and organo-sulfur precipitation [1, 2, 3]. Each will be briefly discussed.

Metal Hydride Reduction

Metals can easily be reduced and precipitated from both organic and inorganic media by reducing agents. Commonly used reducing agents include aluminum, zinc, hydrazine, and a group of reducing agents known as metal hydrides. The most common reducing agent utilized is sodium borohydride. In the application to organomercury compounds, sodium borohydride stabilizes the mercury and removes it from the organic portion of the molecule. Sodium borohydride will reduce the mercury present in thimerosal because the mercury atom is in the +2 oxidation state. The elemental mercury formed as a
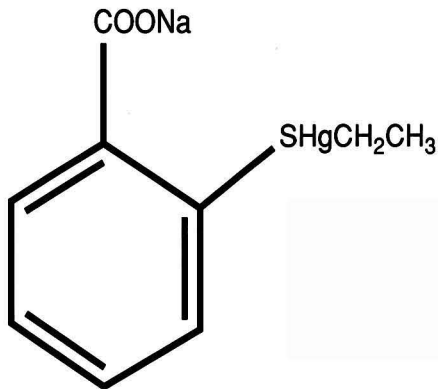
FIGURE 1. Thimerosal (Source: Merck Index, 9th Ed., p. 1,202, 1976)

result of sodium borohydride reduction is in a colloidal state and must be separated from solution by filtration [4].

Free Radical Oxidation

Free radical oxidation fragments large organic compounds into smaller ones. It is the most commonly used method to treat compounds such as phenols and organo metallic compounds that contain metals in a +2 oxidation state. The reagents for this procedure can be ozone or hydrogen peroxide. The use of ultraviolet light or ultrasonics can speed up the rate of reaction. If free radical oxidation of thimerosal goes to completion, the products of the reaction would be water, carbon dioxide, and sulfur compounds containing mercury [5]. If elemental mercury is produced by the reaction, it can be removed by conventional post treatment methods such as sulfide precipitation or ultrafiltration. The high capital costs involved and unproven technology made this a less desirable choice for this application.

Precipitation by Organo-Sulfur Reagents

This technology is used to remove strongly chelated and complexed metal compounds. Precipitation by complex organo-sulfur reagents is similar to conventional sulfide precipitation. Both rely upon the insolubility of mercuric sulfide or mercuri-mercapto compounds to achieve removal of mercury from aqueous waste streams. The organo-sulfur precipitation technology does successfully remove thimerosal from solution. Removal efficiencies were found to be close to 92%. The filter cake from the filtration contains mercury salts up to 10% by weight. This cake, being hazardous and unacceptable for reclamation, would require additional treatment or disposal. Land disposal of mercury is restricted and is not a desired disposal option. The only alternative for the disposal of mercury salts formed from the precipitation reaction would be incineration. Incineration of mercury compounds is not an environmentally sound disposal option as most of it exits in the stack gas as mercury oxides with a small fraction exiting with the incinerator ash [6, 7].

MATERIALS AND METHODS

The at-source treatment for mercury removal from thimerosal is accomplished by aluminum catalyzed reduction at high pH to break the S-H bond. Sodium borohydride is then used to reduce the mercury cations and organomercury fragments to elemental mercury. Ultrafiltration is employed to capture the colloidal metallic mercury. The permeate containing low levels of residual mercury is subjected to tertiary treatment using granular activated carbon. Since most of the thimerosal was found associated with the dead cell mass, caustic hydrolysis is employed to release the biocide.

A. Reagents
1. 12% solution of Sodium Borohydride in a 40% caustic solution. VenMet® solution (Ventron Corporation).
2. Aluminum Metal Powder—Fine (Fisher Scientific, Inc.).
3. Hydrochloric Acid, Concentrated.
4. 50% Sodium Hydroxide Solution.
5. Antifoam B Emulsion (Sigma Chemical Co.).

B. Equipment (Pilot Scale)
1. Ultrafiltration System with 30,000 Molecular Weight Cut Off (30K MWCO) hydrophilic modified regenerated cellulose membrane, #MCR-07 (Bio-Recovery, Inc., Northvale, New Jersey)—A similar membrane may be obtained from other suppliers, e.g. Amicon.
2. F-300 granular activated carbon unit (Calgon Carbon, Pittsburgh, Pennsylvania).

C. Procedure
i) Pretreatment of Cell Paste
1. Add 3N NaOH solution to the cell paste (100 ml/gm), heat to 75°C and stir for 24 hours maintaining a temperature of 75°C to achieve completion of hydrolysis.

ii) Treatment Procedure
1. a. Cell paste: add an amount of aluminum metal powder equivalent to a one-to-one ratio of aluminum to mercury present in the cell paste.
   b. Spent fermentation wastewater: adjust pH to 11.5 with caustic and add an amount of aluminum metal powder at least equivalent to a one-to-one ratio of (weight basis) aluminum to mercury present in the wastewater.
2. Mix for 24 hours.
3. Adjust the pH to 7.0 with concentrated hydrochloric acid.
4. Add VenMet® solution until a pH of 10.0 is obtained and continue intermittent addition of VenMet® solution until the pH is stable at 10.0 for at least five minutes. Note: if solution starts to foam, antifoam/defoamer—e.g. Antifoam B Emulsion, may be added.
5. Mix well for 1 hour.
6. Filter the sample using crossflow ultrafiltration. Filtration parameters—flux 191 liter/meter square/hour at 50 psi. Recycle retentate to achieve a concentration factor of at least 50X.
7. Collect retentate for mercury reclamation.
8. Permeate is passed through a bed of activated carbon (F-300) and the effluent discharged to a holding tank.
9. Upon validation that the mercury content of the effluent in the holding tank is less than 10 μg/l, the effluent is sent to neutralization and equalization before discharge to a wastewater treatment facility.

DISCUSSION

The methodology for the reduction and removal of thimerosal (organo-mercury compound) and plausible reclamation and reuse of mercury, an environmentally sound option, is detailed in the following sections. The process is based on the use of aluminum metal reduction at high pH to break the S-H bond and hydrolyze the organomercury fragments. Sodium borohydride is then used to reduce the mercury cations and organomercury fragments to elemental mercury. The process is described in Section A. Ultrafiltration is then employed to capture the colloidal metallic mercury in the retentate which

FIGURE 2. Flow Sheet for Thimerosal Removal

Waste Stream (100mg/l Hg)
Aluminum Powder
Venmet® Solution (12% Sodium borohydride)

Reaction vessel
Ambient temperature
Cycle time 25 hours

UF

Permeate
Hg. Al.
<150 µg/l

Drums for disposol and reclamation

Concentrate
Hg. Al. Solids

Carbon Bed

Hold Tank

<10 µg/l Hg.

Effluent to Sewer

FIGURE 2. Flow Sheet for Thimerosal Removal

Solids ≈ 1 kg Hg/250 kg cell paste
Digested with NaOH to release bound thimerosal

Aqueous Waste Stream
Volume = 3800 l
Hg = 100 mg/l; 380 g
SS = 1200 mg/l; 4.56 kg
TS = 2360 mg/l; 8.97 kg

Aluminum Powder
Al = 100 mg/l; 380 g

Venmet® Solution
(45-50 L, 12% NaBH₄ in Caustic)

Reactor
5678 Liters
T= Ambient
Rxn time ≈ 25 hr

UF Membrane: 30,000 MWCO # MRC-07
(Modified Regenerated Cellulose)
Highly hydrophilic, Easy to clean. Area = 3M²
Filtration ≈ 5 hrs.: Flux 191 (Lit/M²/hr) @ 50 psi

50 X Concen.

Retentate - Reclaim Hg
Volume = 380 l/wk
Hg = 5 G/L; 380 g
Al = 5 G/L; 380 g
SS = 60 G/L; 4.56 kg
TS = 118 G/L; 8.97 kg

Permeate   (3724 l/wk)
Hg = 150 µg/l; 0.56 g
Al <50 µg/l; <0.2 g

Final Polishing Using
Granular Activated Carbon

Effluent
3724 l/week; Al < 10 µg/l
Hg < 10µg/l

Hg Drinking Water Standard = 2 µg/l

Sewer

**FIGURE 3. Material Balance for Large-Scale Application
of the Developed Technology**

Table 1 Chemistry of the Method

Step I.   Treatment with Al

$$Al:Hg = 1:1, \ pH = 11.5, \ t = 24 \ hrs.$$

THE ALUMINUM ACTS AS A REDUCING AGENT

$$Al \longrightarrow Al^{+3} + 3e^-$$

THE REDUCTION INVOLVES ONE OR MORE OF THE
FOLLOWING REACTIONS:

$$1. \ 2e^- + RSH_gEt + 2H_2O \longrightarrow RH + HSH_gEt + 2OH^-$$

$$2. \ 2e^- + RSH_gEt + H_2O \longrightarrow RH + HOHH_gEt + S^{-2}$$

$$3. \ 4e^- + RSH_gEt + 2H_2O \longrightarrow RH + [HH_gEt] + S^{-2} + 2OH^-$$

Step II.   Treatment with Sodium Borohydride

$$@ \ pH = 10$$

$$4 \ Hg^{+2} + NaBH_4 + 8OH^- \longrightarrow 4Hg + NaBO_2 + 6H_2O$$

Note: Organo mercury fragments undergo base catalyzed hydrolysis in Step I. The resultant smaller organo mercury fragments are reduced to form Hg ions. The final reduction of ionic Hg to elemental mercury is accomplished in Step II.

can be collected and sent offsite for reclamation and non-process reuse; the specifics are outlined in Section B. The transparent, clear and sparkling permeate was passed through a fixed-bed of granular activated carbon. The GAC provides tertiary treatment to remove residual Hg from the UF permeate and produces an effluent with a mercury concentration of less than 10 $\mu g/l$. The details are furnished in Section C.

A detailed kinetic evaluation was not performed. However, the laboratory experiments furnish qualitative/semi-quantitative kinetic information as outlined in Section D. Comments as to heat effects and hydrogen gas generation are given in Sections E and F, respectively. Most of the biocide has been found to be associated with the dead cell mass and, hence, necessitated the release of bound thimerosal from cell paste before sodium borohydride reduction. The details of caustic hydrolysis of cell paste to release the thimerosal are discussed in Section G. The flowsheet and material balance for a proposed large-scale application of the technology are shown in Figures 2 and 3.

SECTION A.   PROCESS CHEMISTRY: ALUMINUM POWDER AND SODIUM BOROHYDRIDE REDUCTION

The chemistry of the method is shown in Table 1. Aluminum powder is used to desulfurize the organosulfur bond. A catalytic amount of aluminum is required. The minimum charge was found to be one gram of aluminum powder for each gram of mercury present. Use of excess aluminum has been found not to increase the reaction rate. The base catalyzed hydrolysis, using caustic, is carried out at a pH of 11.5. The reaction is heterogeneous and requires 24 hours to reach completion. During the reaction, a substantial amount of the organic material present in the waste undergoes hydrolysis.

Sodium borohydride in a stabilized alkaline solution containing 12% NaBH₄, 42% NaOH, and the remainder water is used in this process. In organomercury applications, once the S-Hg bond is broken, the sodium borohydride will stabilize the mercury and cleave it from any remaining organic portions of the molecule. The mercury ions thus formed can then be reduced to the elemental state directly by sodium borohydride. In theory, the amount of sodium borohydride added is based on the ability of sodium borohydride to donate 8 electrons. A mercuric cation requires two electrons to be completely re-

Table 2 Performance of Cross-Flow Ultrafiltration Membrane and Granular Activated Carbon Bed
Initial Hg Concentration in the Wastewater = 56 mg/l

MWCO (K)	Type*	Flux-LMH @50 psi	Concent. (X)	Ease of Cleaning	Hg in Permeate $\mu g/l$	Hg After Post Treat., with GAC $\mu g/l$	Rem Eff, %
30	1	119	100	No	110	2	>99.99
30	2	191	100	Yes	110	2	>99.99
80	3	200	100	No	150	5	>99.99
100	4	119	100	No	180	5	>99.99
100	5	119	100	No	210	3	>99.99

*Membrane type
1. Slightly hydrophilic, polysulfone
2. Most hydrophilic, modified regenerated cellulose
3. Most hydrophobic, polysulfone
4. Slightly hydrophobic, polysulfone
5. Slightly hydrophilic, polysulfone

duced. Therefore, one molecule of sodium borohydride can theoretically reduce four mercuric ions to the elemental state.

$$4\,Hg^{+2} + NaBH_4 + 8\,OH^- \longrightarrow 4\,Hg^0 + NaBO_2 + 6\,H_2O$$

In practice, the actual amount of sodium borohydride added is variable due to the various oxidation states of the mercury cations present in the waste stream. It is also dependent on the amount of organomercury fragments and other organic/inorganic compounds present in the wastewater which can undergo reduction. All of these contribute to the sodium borohydride demand. The amount of sodium borohydride required for the complete reduction of mercury can be monitored by pH measurement. The reduction reaction reaches completion when the pH of the wastewater is brought to 10 and remains stable at pH 10.0 for at least ten minutes without a need for further addition of sodium borohydride solution. As sodium borohydride is consumed, the pH of the solution will decrease. Therefore, a stable pH reading of 10 indicates that the reaction has gone to completion. The treated wastewater is stirred for one hour and the colloidal mercury is separated by ultrafiltration.

SECTION B. ULTRAFILTRATION

The ultrafiltration system used was of plate and frame design and is manufactured by Bio-Recovery, Inc., Northvale, New Jersey. The lab unit can be directly scaled up to a larger pilot plant unit. A 30K MWCO—modified regenerated cellulose

membrane, #MCR07 (the most hydrophilic membrane tested) was found to give the best overall performance. The membrane yielded a flux of 191 liters/meter square/hour at 50 psi. The membrane was easily cleaned by running a 0.5N NaOH solution through the system for 15 minutes. There was no evidence of decreased flux in filtration before and after multiple uses following cleaning. Visual inspection indicated negligible change in morphology of the membrane. The membrane was used for three consecutive runs with no loss of membrane performance. After the final run, the membrane was cleaned and again visually inspected; it looked morphologically very similar to a new membrane. There was no discoloration or evidence of damage due to abrasion, etc.

The permeate was assayed for mercury content and found to contain 110 $\mu g/l$ of mercury. The initial mercury concentration of the waste was 56 mg/l. Therefore, the removal efficiency of the ultrafiltration membrane (#MCR07) is 99.7%. Other membranes were also evaluated and their performance is summarized in Table 2.

SECTION C. POLISHING OF ULTRAFILTRATION PERMEATE USING GRANULAR ACTIVATED CARBON

The permeate from the ultrafiltration was passed through a fixed bed granular activated carbon filter. F-300 GAC, avail-

Table 3 GAC Treatment to 10 Liters of UF Permeate Containing 56 mg/l Hg (100K MWCO/hydrophilic)

Total Volume	Color of Permeate from GAC	Mercury, mg/l
1 liter	clear, no amber color detected	<0.01
2 liters	clear, no amber color detected	<0.01
3 liters	slight amber color detected	<0.01
4 liters	slight amber color detected	<0.01
5 liters	slight amber color detected	<0.01
6 liters	slight amber color detected	<0.01
7 liters	amber color	<0.01
8 liters	amber color	<0.01
9 liters	amber color	>10.0*
10 liters	amber color	>10.0*

*indicates saturation of the bed

Table 4 Total Organic Carbon Removal by the GAC Bed from the UF Permeate

Sample	Membrane	TOC of UF Permeate "as is" mg/l	TOC after "GAC" mg/l	% TOC Removal by GAC
1	30K/MWCO mod. regen. cel./#MRC07	8,900	4,175	53
2	80K/MWCO polysulfone/ #PS012	11,150	4,100	63.2
3	100K/MWCO polysulfone/ #PS007	15,570	4,825	69.0
4	100K/MWCO polysulfone/ #PSH07	15,975	11,175	30.0

able from Calgon Carbon, is recommended. A 4.5% maximum loading of mercury has been determined for the F-300 GAC. A pH of 10 is required for maximum mercury adsorption. Less than 10 $\mu g/l$ of mercury was detected in the effluent after the GAC filtration/polishing step (refer to Table 2).

The adsorption of thimerosal onto carbon depends on three factors: 1. the solubility of thimerosal, 2. the pH of the wastewater stream, and 3. the presence of other compounds in the wastewater stream which may interfere with the adsorption/solubility of thimerosal. Usually, the more soluble a compound is, the less likely it will be adsorbed onto carbon. Thimerosal is a very soluble compound and, therefore, is only slightly adsorbable on carbon. Mercury metal is highly adsorbed on the carbon and experimental results at different carbon loadings are shown in Table 3.

The following experiment was utilized to determine the mercury loading on the carbon before breakthrough. The permeate contained soluble organics. Literature indicates that soluble organics are not retained well on GAC at a pH of 10.0, which is the optimal pH for mercury adsorption. A 9 cm funnel was utilized as a support for 10 grams of Calgon F-300 GAC. Hg was added to the treated UF (#PSH07, 100K MWCO) permeate to result in a 56 mg/l solution which was utilized for breakthrough experiments. A total of 10 liters was passed through the carbon bed. The data indicate mercury breakthrough at 4.5% loading. This is similar to the results obtained in previous experiments. The organics, thus, do not interfere in the adsorption of the mercury on the carbon. The data are furnished in Table 4.

SECTION D. KINETICS

Kinetic parameters were not specifically evaluated in this study. However, some information of a qualitative nature is available from the laboratory experiments. The concentration of aluminum powder required for the metal hydride reduction of the S-Hg bond was investigated. The data indicate that an aluminum to mercury ratio of 1 to 1 (weight basis) is required. This catalytic amount of aluminum is required for the reaction to go to completion within 24 hours. The initial ratio tested, based on the literature reported procedure, was 250 to 1. Excess aluminum has been found to not interfere in the reaction. Ratios less than 1 to 1 produced incomplete reduction reactions.

The time required for the reaction to reach completion for

Table 5 Caustic Hydrolysis (3N NaOH) of Cell Paste: Effect of Temperature and Time on Bound Thimerosal (Hg)

		Hg IN SOLUTION		
EXPT NO	TIME (HOURS)	25°C Hg (mg/l)	50°C Hg (mg/l)	75°C Hg (mg/l)
1	0	0.00	0.0	0.0
2	1	5.33	23.5	30.3
3	2	16.00	25.3	30.8
4	4	22.10	25.5	31.1
5	6	35.30	31.5	35.5
6	8	30.80	35.3	35.9
7	12	33.50	38.8	41.1
8	24	40.30	40.5	42.0
Hg in Initial Solids (g)		43.4	43.4	43.4
Hg in Final Solids (g)		3.6	1.1	0.6
Hg in Liquid Phase (g)		39.8	42.3	42.9
% Hg in Liquid Phase (g)		91.7	97.5	98.8
% Hg Recovery		100.0	100.0	100.2
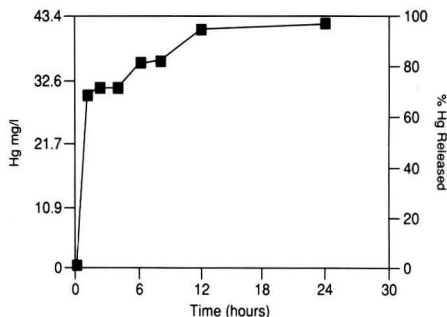
FIGUE 4. Release of Mercury from Cell Paste into Liquid Phase @75°C, 3N NaOH

aluminum-to-mercury ratio of 1 to 1 was also investigated. The data indicate that a minimum reaction time of 18 hours is required under these conditions. This was experimentally determined by exploiting the property that thimerosal does not readily adsorb onto carbon. The volume of solution to mass of carbon was kept constant throughout the experiments. Mercury loading was also kept below the breakthrough concentration except when breakthrough was evaluated.

SECTION E. HEAT EFFECTS

The overall heat of reaction was monitored in the pilot scale runs (57 liters each). Batch-to-batch variability in the buffering capacity of the spent fermentation broth resulted in marked differences in the amount of caustic required for pH adjustment of the wastewater. The overall heat of reaction was much greater for the first run than the second. The data given below are for the first pilot scale batch (worst case). The initial pH adjustment with 50% caustic resulted in a 4.2°C increase in temperature. No heat of reaction was observed after the addition of aluminum powder or during the 24-hour period the solution was mixed with the aluminum powder. The second adjustment of pH to 7.0 with concentrated HCl resulted in a 6.0°C increase in temperature. The addition of sodium borohydride solution was accompanied by a small heat of reaction (0.5°C). The total increase in temperature resulting from the overall heats of reactions is 10.7°C. It should be noted that the reported temperature increases were obtained under nonadiabatic conditions.

SECTION F. HYDROGEN GAS GENERATION

Sodium borohydride is unstable at low pH (below pH 7.0). At pH less than 7.0, the compound undergoes hydrolysis and hydrogen gas is evolved. In the proposed process, the pH of the solution to which sodium borohydride is added is adjusted with concentrated hydrochloric acid to a pH of 7.0. Thus, the amount of hydrogen gas evolved is minimized; however, venting of the vessel is recommended so as to allow any hydrogen gas evolved to be removed safely. At pH less than 7.0, the following hydrolysis reaction is favored:

$$BH_4^- + 4H_2O \longrightarrow B(OH)_3 + OH^- + 4H_2$$

SECTION G. CELL PASTE

The material balance data indicate that greater than 50% of the thimerosal is associated with the dead cell mass. The cell paste requires 3N NaOH and heating at 75°C for 24 hours to solubilize most of the thimerosal for further treatment

(Table 5). The release of mercury from cell paste into liquid phase as a function of time at 75°C is shown in Figure 4. The hydrolyzed cell debris contain little if any mercury and, therefore, the cell paste is amenable to treatment by this process.

CONCLUSION

An environmentally sound waste minimization approach which utilizes an at-source treatment technology for the removal and recovery of mercury from a spent fermentation waste to render it non-hazardous was developed. The organomercury-containing fermentation wastewater is initially treated with aluminum metal powder at pH 11.5 and ambient temperature to reduce the sulfur-hydrogen bond to form mercury cations and organomercury fragments. Since most of the biocide has been found associated with the cell mass, caustic hydrolysis is used to release the organomercury compound from cell paste before treatment. Subsequent treatment with sodium borohydride reduces the mercury cations to the colloidal metal. Ultrafiltration effectively removes the colloidal metallic mercury. Final polishing with granular activated carbon yields a transparent, clear and sparkling effluent containing less than 10 μg/l mercury. The colloidal Hg present in the UF retentate as well as bound to granular activated carbon is amenable to reclamation and subsequent reuse. The process has been designed so as to mitigate heat effects and hydrogen gas generation.

The at-source treatment technology developed is capable of achieving a consistently high removal efficiency of 99.99%, thus, providing an environmentally sound option for mercury reclamation and reuse. As has been the experience with other processes, this provides yet another classic example of a process related waste minimization opportunity.

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Biotreatment of Hazardous Organic Wastes Using Rotating Biological Contactors

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Treatment of several toxic organic compounds in Rotating Biological Contactor (RBC) units was examined in this study. The following compounds were included: 2-Chlorophenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol; pentachlorophenol; 2-nitrophenol; diethyl phthalate and di-n-butyl phthalate.

INTRODUCTION

Phenolic compounds present in various industrial wastewater discharges are highly toxic and pose a direct threat to humans and aquatic life. 2-Chlorophenol and 2,4-dichlorophenol have extremely low odor threshold in water, therefore, their presence may interfere with the beneficial uses of water. 2,4-Dichlorophenol and 2,4,6-trichlorophenol are used in the manufacture of industrial and agricultural products such as pesticides, germicides, soil sterilants, seed disinfectants and antiseptics. They are also used widely as an intermediate in the production of pentachlorophenol, a wood preservative [1]. Pentachlorophenol is a very potent chemical and used as a bactericide, herbicide or insecticide. 2-Nitrophenol may also be used in the synthesis of pesticides and other intermediates including dyestuffs.

Phthalate esters are used extensively in the manufacture of plastics such as polyvinyl chloride (PVC). By serving as plasticizers, they provide the flexibility of the products and improve their workability. Some plastic formulations may contain up to 60 percent phthalate esters. Phthalate esters are suspected of being carcinogenic, teratogenic, mutagenic, toxic and the cause of other health effects such as reproductive system disorders; eye, nose, throat and upper respiratory tract irritation; and nausea [1, 2].

There have been considerable contributions to the knowledge on RBC technology over the last decade. The literature, however, contains limited information on the RBC treatability of toxic organic wastes. A review of literature shows that a major portion of the studies on the biological treatment of chlorinated phenols and phthalate esters is sponsored by the U.S. Environmental Protection Agency (EPA). For example, H. Tabak of EPA and his coworkers [3] examined the biodegradability of various organic hazardous compounds. Their list included the phenols and phthalate esters studied in this study.

Tischler and Kocurek [4] examined the effectiveness of biological treatment in removing toxic organic pollutants from chemical industry wastewaters. Operational data from activated sludge treatment systems operated by five organic chemicals manufacturing plants were compiled and evaluated. Sixty toxic organic pollutants including 2-chlorophenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol; pentachlorophenol; 2-nitrophenol; diethyl phthalate and dibutyl phthalate were detected in wastewater samples. The average removal rates for these compounds were: 2-Chlorophenol, 41 percent; 2,4-dichlorophenol, 91 percent; 2,4,6-trichlorophenol, 45 percent; pentachlorophenol, 36 percent; diethyl phthalate, 99 percent; and dibutyl phthalate, 99 percent.

Table 1 Synthetic Wastewater Composition

Compound	Concentration, mg/L*
Glucose	210
Powdered milk	110
Peptone	25
Ethylene glycol	0.05 mL/L
Ethyl alcohol	0.01 mL/L
Ammonium sulfate	80
Ammonium chloride	5
Magnesium sulfate	10
Manganese sulfate	3
Calcium chloride	3
Ferric chloride	0.3
Potassium phosphate (monobasic)	14
Potassium phosphate (dibasic)	28

*Except as noted

Table 2 The Response of Unit 1 to 2-Nitrophenol

Average Influent 2-Nitro-phenol conc., mg/L	Average Effluent 2-Nitro-phenol conc., mg/L	Percent 2-Nitro-phenol removal	Average Influent COD, mg/L	Average Effluent COD, mg/L	Percent COD Removal
0.29	0.01	96.6	464	55	88.1
0.46	0.02	95.7	459	46	90.0
0.58	0.02	96.6	426	37	91.3
0.82	0.03	96.3	449	58	87.1
1.09	0.11	89.9	444	38	91.4
1.31	0.10	92.4	451	41	90.9
2.47	0.29	88.3	419	41	90.2
5.45	0.48	91.2	465	37	92.0
5.56	0.44	92.1	464	36	92.2
6.21	0.36	94.2	462	52	88.7
6.78	0.56	91.7	478	43	91.0
7.58	0.77	89.8	436	59	86.5
8.08	0.85	89.5	438	43	90.2
8.18	0.61	92.5	428	44	89.7
11.17	0.72	93.6	459	55	88.0

There are a limited number of reports available on the RBC treatment of industrial wastewaters. For example, Congram [5] studied the treatment of petroleum refinery wastewaters using a 4-stage RBC. He reported that the influent and effluent phenol concentrations were 2.65 and 0.12 mg/L, respectively, which is equivalent to a removal efficiency of 95.5 percent.

More recently, Huang, et al. [6] studied the RBC treatment of phenol-formaldehyde resin wastewaters. Pilot-scale RBCs and various influent phenol levels (in some cases as high as 600 mg/L) were used in this study. Results showed that average phenol removal rates were above 99 percent, and COD removal efficiencies varied from 67 to 83 percent.

Davis and Pankratz [7] studied the RBC treatment of process wastewater from a petrochemical plant. They used a 4-stage, pilot-scale system with 4-ft diameter discs. They obtained the following removal rates: TOC, 38 percent; COD, 47 percent; and phenols, 89 percent. When preaeration was added to the system, TOC removal increased to 45 percent, and similarly, COD and phenols removal rates were higher at 67 and 98 percent, respectively.

MATERIALS AND METHODS

Two pilot-scale RBC units with 0.5 m diameter discs were used. The discs of the units were made of high density polyethylene and arranged in four stages. The rotational speed of the discs was 4 rpm. The total surface area of the discs was approximately 250 ft^2 (23.2 m^2) and the liquid capacity of the system was slightly below 140 liters. The hydraulic loading of the system was maintained at 1.5 gal/day per sq ft (except when the effects of hydraulic loading variations were studied). At a hydraulic loading of 1.5 gal/day per sq ft the hydraulic retention time was about 2.4 hours. The organic loading was kept at 6.0 lb COD/day per 1000 sq ft of the disc surface area. A synthetic wastewater (Table 1) was used. Activated sludge from a local municipal wastewater treatment plant and watermud mixture taken from a pond were used as the seed. The biofilm was allowed to form on discs for a period of over three months before the addition of toxic compounds. The following analyses were performed daily: Influent COD, filtered effluent COD, influent and effluent chlorinated phenol and/or 2-nitrophenol, and phthalate ester concentrations, effluent suspended solids, and pH. Analytical techniques described in Standard Methods [8] and EPA Methods 604 and 606 [9] were followed.

RESULTS AND DISCUSSION

The response of RBC units to 2-chlorophenol and 2-nitrophenol was examined during the initial phase of this study. Unit 1 received synthetic waste containing gradually increasing levels of 2-nitrophenol, and 2-chlorophenol was added to the influent of Unit 2. During the period Day 60–Day 76, Unit 1 received increasing levels of 2-chlorophenol in addition to approximately 11 mg/L of 2-nitrophenol. Tables 2 through 4 and Figures 1 through 3 illustrate the response of the RBC units to increasing 2-nitrophenol and 2-chlorophenol concentrations. It was observed that throughout this phase of the study, the removal efficiency for 2-nitrophenol was high and consistently near or above 90 percent (Unit 1). Similarly, COD removal rates for Unit 1 seldomly fell below 90 percent.

Table 3 The Response of Unit 2 to 2-Chlorophenol

Average Influent 2-Chloro-phenol conc., mg/L	Average Effluent 2-Chloro-phenol conc., mg/L	Percent 2-Chloro-phenol removal	Average Influent COD, mg/L	Average Effluent COD, mg/L	Percent COD Removal
0.33	0.16	51.5	449	52	88.4
0.64	0.47	26.6	419	47	88.8
0.89	0.51	42.7	436	62	85.8
1.45	1.25	13.8	412	63	84.7
2.66	2.53	4.9	455	57	87.5

Table 4 Removal of 2-Chlorophenol and 2-Nitrophenol in Unit 1

Period	Average Influent 2-Chlorophenol conc., mg/L	Average Effluent 2-Chlorophenol conc., mg/L	Percent 2-Chlorophenol removal	Average Influent 2-Nitrophenol conc., mg/L	Average Effluent 2-Nitrophenol conc., mg/L	Percent 2-Nitrophenol removal
Day 60–Day 65	0.52	0.48	7.7	11.09	0.79	92.9
Day 66–Day 76	3.29	2.66	19.1	11.47	0.61	94.7
Day 71–Day 75*	3.44	2.40	30.2	11.60	0.59	94.9

*The highest 2-chlorophenol removal efficiency was obtained during the period Day 71–Day 75
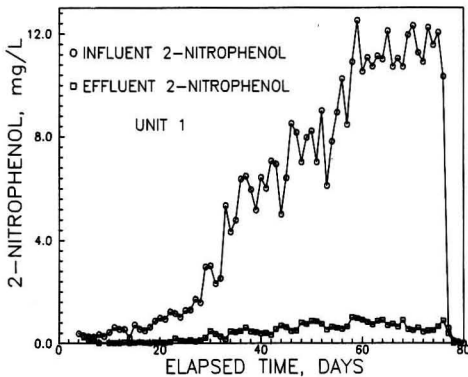
FIGURE 1. Response of Unit 1 to increasing concentrations of 2-nitrophenol.
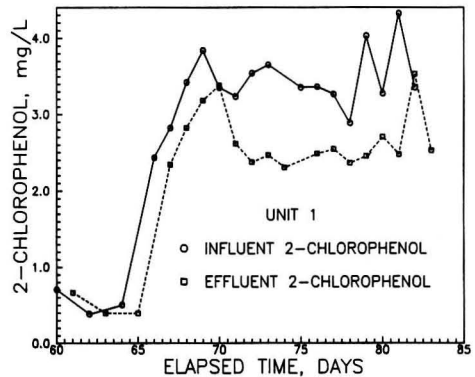
FIGURE 3. Removal of 2-chlorophenol in Unit 1 (in the presence of 11 mg/L 2-nitrophenol).

Removal rates for 2-chlorophenol were lower, and the highest removal obtained during this phase was 51.5 percent which occurred when the influent concentration was 0.33 mg/L (Unit 2). However, later during this study, 2-chlorophenol removal efficiencies improved. The inclusion of both 2-chlorophenol and 2-nitrophenol in the same RBC unit did not affect these results; 2-nitrophenol removal efficiency remained high while the highest removal obtained for 2-chlorophenol was about 30 percent which occurred briefly (Day 71–Day 75) (Table 4).

Highly chlorinated phenols are reported to be more resistant to microbial degradation [1, 3], therefore, the synthetic wastewater for Unit 1 was spiked in the following order: 2-Chlorophenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol and finally pentachlorophenol. An initial 2-chlorophenol concentration of less than 1 mg/L (Day 60) was increased gradually and was maintained at about 3.5 mg/L throughout the study. Acclimation to 2-chlorophenol was slow, an examination of Figure 4 shows that effluent concentrations of 2-chlorophenol gradually diminished, and for the period Day 97 through Day
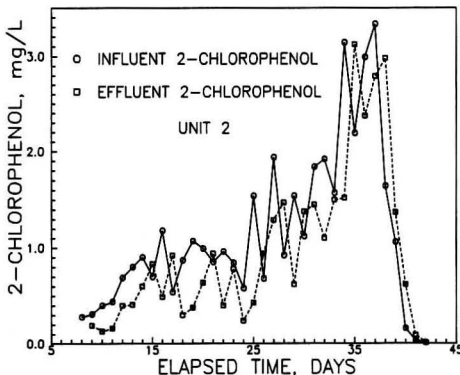
FIGURE 2. Response of Unit 2 to increasing concentrations of 2-chlorophenol.
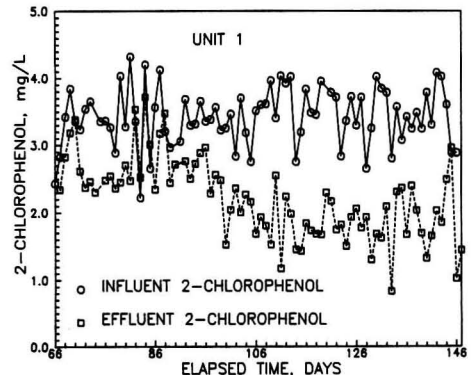
FIGURE 4. Acclimation of Unit 1 to 2-chlorophenol.

Table 5 Calculation of 2-Chlorophenol Removal Efficiency

Period	Average Influent Conc., mg/L	Number of Data	Standard Deviation	Average Effluent Conc., mg/L	Number of Data	Standard Deviation	Percent Removal
Day 96–Day 147[a]	3.45	50	0.39	1.89	51	0.43	45.2
Day 105–Day 131[b]	3.51	25	0.42	1.79	26	0.31	49.0
Day 66–Day 147[c]	3.42	78	0.43	2.20	79	0.60	35.7

[a]Data from the acclimation period are excluded
[b]The period of highest 2-chlorophenol removal
[c]Data from the acclimation period are included

Table 6 Calculation of 2,4-Dichlorophenol Removal Efficiency

Period	Average Influent Conc., mg/L	Number of Data	Standard Deviation	Average Effluent Conc., Mg/L	Number of Data	Standard Deviation	Percent Removal
Day 96–Day 147[a]	9.37	51	1.16	2.44	51	0.83	74.0
Day 89–Day 147[b]	9.31	58	1.12	3.00	58	1.74	67.8

[a]Data from the acclimation period are excluded when computing the average values and standard deviations
[b]Data from the acclimation period are included
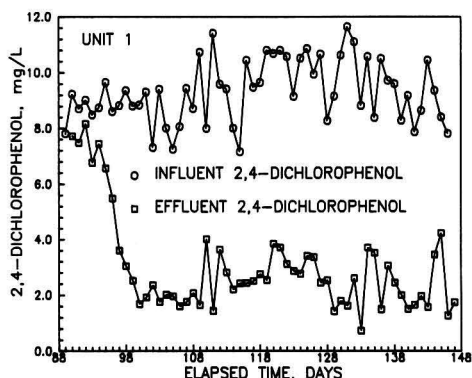
FIGURE 5. Response of Unit 1 to 2,4-dichlorophenol.
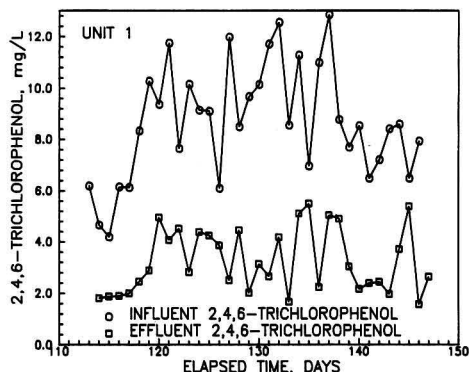
FIGURE 6. Removal of 2,4,6-trichlorophenol in Unit 1.

Table 7 RBC Treatability Data for Chlorinated Phenols

Compound	Average Influent Conc., mg/L	Number of Data	Standard Deviation	Average Effluent Conc., mg/L	Number of Data	Standard Deviation	Percent Removal
2-Chlorophenol	3.42	78	0.43	2.20	79	0.60	35.7
2,4-Dichlorophenol	9.31	58	1.12	3.00	58	1.74	67.8
2,4,6-Trichlorophenol	8.65	34	2.22	3.25	34	1.25	62.4
Pentachlorophenol	3.46	12	1.35	1.64	12	0.57	52.6
COD	468	81	36	60	81	21	87.2
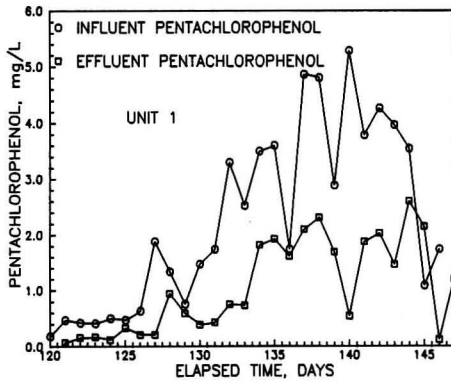
FIGURE 7. Response of Unit 1 to pentachlorophenol.

FIGURE 8. Unit 1 influent and effluent COD data (Days 60–146).

147, the average effluent concentration was about 1.90 mg/L compared to a mean effluent value of 2.76 mg/L for Day 67 through Day 96. The 2-chlorophenol removal efficiency for the entire period was computed as 35.7 percent (Table 6).

Approximately 0.3 mg/L of 2,4-dichlorophenol was added to Unit 1 on Day 74. Over the two-week period that followed, the influent concentration was gradually increased to above 9 mg/L, with a target level of about 10 mg/L. Figure 5 shows the response of the system to 2,4-dichlorophenol. Once again, a distinct acclimation period is observed (Days 90 through 100), with the effluent concentration dropping from 8 mg/L on Day 90 to 2 mg/L on Day 100. The average influent and effluent 2,4-dichlorophenol concentrations over the period Day 89–Day 147 were 9.31 and 3.00 mg/L, respectively; which translates to an average removal rate of 67.8 percent (Table 7).

2,4,6-Trichlorophenol was added to the system on Day 96 at a level of about 0.3 mg/L, with its concentration gradually increasing to about 10 mg/L on Day 119 (Figure 6). The average influent and effluent concentrations for 2,4,6-trichlorophenol,

Table 8 Conversion Table

Gal/ft²/day	m³/m²/day
1.0	0.04
1.5	0.06
1.75	0.07
2.0	0.08

Table 9 Influent and Effluent Data for Various Hydraulic Loadings

Hydraulic Loading, gal/sq ft per day	Average Influent Conc., mg/L	Number of Data	Standard Deviation	Average Effluent Conc., mg/L	Number of Data	Standard Deviation
(a) 2-Chlorophenol						
1.0	5.56	9	0.52	1.77	8	1.01
1.5	3.78	5	0.35	1.36	5	0.83
1.75	2.96	5	0.26	1.07	5	0.31
2.0	2.95	9	0.21	1.11	9	0.49
(b) 2,4-Dichlorophenol						
1.0	13.87	10	1.92	1.57	9	1.03
1.5	10.16	5	1.21	1.99	5	1.20
1.75	7.71	5	0.61	1.60	5	0.40
2.0	7.17	9	0.50	2.15	9	0.80
(c) 2,4,6-Trichlorophenol						
1.0	14.46	10	2.26	2.85	9	1.67
1.5	11.09	5	2.13	4.17	5	2.32
1.75	7.89	5	1.29	2.98	5	0.62
2.0	7.41	9	1.18	3.44	9	1.12
(d) Pentachlorophenol						
1.0	12.21	10	4.81	2.97	9	1.73
1.5	8.88	5	3.27	3.86	5	2.03
1.75	7.03	5	0.93	3.43	5	0.92
2.0	7.22	9	1.43	3.72	9	1.23
(e) COD						
1.0	725	10	66	159	10	47
1.5	527	5	111	114	5	51
1.75	463	5	18	107	5	20
2.0	463	9	13	118	9	30

Table 10 The Effect of Hydraulic Loading Variations on Chlorinated Phenols and COD Removal Efficiencies (in percent)

Hydraulic Loading, gal/sq ft per day	2-Chloro-phenol	2,4-Di-chloro-phenol	2,4,6-Tri-chloro-phenol	Penta-chloro-phenol	COD
1.0	68.2	88.7	80.3	75.7	78
1.5	64.0	80.4	62.4	56.5	78
1.75	63.9	79.2	62.2	51.2	77
2.0	62.4	70.0	53.6	48.5	73
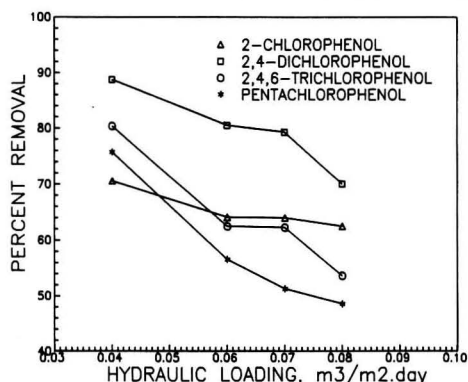
FIGURE 9. The effect of hydraulic loading variations on the chlorinated phenol removal efficiencies.

Day 113 through Day 147, were 8.65 and 3.25 mg/L, respectively, with an average removal efficiency of 62.4 percent (Table 7).

Pentachlorophenol was added to the influent last, Day 120 through Day 147. An initial concentration of less than 1 mg/L was increased gradually to about 4 mg/L (Figure 7). The average influent and effluent concentrations for the period Day 135–Day 147 were 3.46 and 1.64 mg/L, respectively, yielding an average removal rate of 52.6 percent (Table 7).

The acclimation trend (that is gradual decrease in the effluent chlorinated phenol concentration) observed for 2-chlorophenol and 2,4-dichlorophenol was nonexistent for 2,4,6-trichlorophenol and pentachlorophenol. The effluent concentrations seemed to follow the variations in the influent levels instead.

Throughout this phase of the study, (Day 66–Day 147), the influent COD varied between a minimum of 365 mg/L and a maximum of 631 mg/L. The mean influent COD was 468 mg/L. The effluent COD varied between 24 and 132 mg/L with an average value of 60 mg/L (Figure 8 and Table 7). The average COD removal efficiency for this phase of the study was 87.2 percent. The overall performance of the RBC system for the treatability of chlorinated phenols is summarized in Table 7.

In the next phase of the project, the effect of the hydraulic loading variations on the RBC treatability of chlorinated phenols was examined. Hydraulic loading was first decreased from 1.5 gal/sq ft per day to 1.0 gal/sq ft per day (Day 147), then it was increased to 1.5 (Day 157), 1.75 (Day 162), and 2.0 gal/sq ft per day (Day 167) (see Table 8 for conversion to SI units). As it was noted earlier, the organic loading was kept at 6.0 lb COD per 1000 sq ft of the disc surface area per day throughout the study. The response of the system is presented in Tables 9 and 10 and Figure 9. At the beginning of this phase, when the hydraulic loading was reduced to 1.0 gal/sq ft per day, the chlorinated phenol efficiencies showed considerable improvement. For example, pentachlorophenol removal rate increased from 52.6 to 75.7 percent. Similarly, the removal efficiencies for other chlorinated phenols improved as follows: 2,4,6-Trichlorophenol, 62.4 to 80.3 percent; 2,4-dichlorophenol, 67.8 to 88.7 percent; 2-chlorophenol, 35.7 to 68.2 percent. Removal efficiencies dropped when the hydraulic loading was increased back to 1.5 gal/sq ft per day, however, the removal rates obtained were higher than those observed earlier. Additional increases in hydraulic loading led to further drops in the removal efficiencies. A comparison of the lowest and the highest removal rates shows that pentachlorophenol and 2,4,6-trichlorophenol removal rates were affected the most. The stepwise increase in the hydraulic loading from 1.0 to 2.0 gal/sq ft per day resulted in about 27 percentage points drop in the removal efficiencies of pentachlorophenol and 2,4,6-trichlorophenol. The decrease for 2,4-dichlorophenol and 2-

Table 11 Influent and Effluent Phthalate Esters and COD Data

Period	Average Influent Conc., mg/L	Number of Data	Standard Deviation	Average Effluent Conc., mg/L	Number of Data	Standard Deviation
			(a) Diethyl Phthalate			
Day 13–Day 21	13.93	9	2.57	0.94	3	0.48
		Removal Efficiency = 93.3 %				
			(b) Dibutyl Phthalate			
Day 26–Day 78	5.72	39	3.17	1.97	48	1.07
		Removal Efficiency = 65.6 %				
			(c) COD			
—	561	75	80	69	78	19
		Removal Efficiency = 87.7 %				

chlorophenol were 18.7 and 5.8 percentage points, respectively (Table 10).

While RBC Unit 1 was being used to study the treatability of 2-nitrophenol and chlorinated phenols, phthalate esters were being added to Unit 2 to study their RBC treatability. Diethyl phthalate was added to Unit 2 first, followed by dibutyl phthalate. For diethyl phthalate, treatment efficiency calculations yielded 93.3 percent removal (Table 11). Similar calculations for dibutyl phthalate resulted in an average removal rate of 65.6 percent, based on the data shown in Table 11. The COD data for Unit 2 are also presented in Table 11.

CONCLUSIONS

The treatability data for phenols compiled during this study compare favorably with the biological treatability data reported in the literature and summarized in this report.

Based upon the results obtained, it is concluded that RBC is a viable treatment process for 2-nitrophenol and chlorinated phenols (2-chlorophenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol; and pentachlorophenol) containing wastes.

Hydraulic loading rate and hydraulic retention time are important process parameters for RBC design and operation, and when they are varied, the removal efficiencies will be affected.

ACKNOWLEDGEMENT

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Full-Scale Remediation of a Grey Iron Foundry Waste Surface Impoundment

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A large grey iron foundry was facing remediation of a surface impoundment containing approximately 300,000 cubic yards of EP-Toxic sludge. The sludge was generated by the settling of wastewater solids from air emission control systems connected with cupola melting operations. Bench-scale treatability testing was used to evaluate various chemical treatment possibilities for rendering the sludge non-EP-Toxic. Several phosphate sources and different engineering options were evaluated for cost-effectiveness of full-scale remediation. The most economical option was to dredge the solids continuously as a slurry (while the impoundment remained in operation) with injection of phosphoric acid into the slurry pipeline. The treatment process was controlled by monitoring residual phosphate in the treated slurry. The remediation process was tested in a month-long field trial using full-scale equipment, and was followed by successful remediation during a 6-month period. A technical overview and performance data on the remediation process are presented.

INTRODUCTION

A large Midwestern foundry uses a wet cap and venturi scrubber system to collect particulate emissions from the cupola melting operations. Wastewater solids settle in a 17-acre surface impoundment, and the effluent liquid is reused in the plant. The accumulated sludge in the impoundment has been periodically removed by hydraulic dredging, and disposed in an on-site, state-approved, solid waste landfill.

Previous testing of the wet cap and scrubber emissions near the point of origin documented that they did not release metals above the RCRA EP Toxicity criteria. However, in the process of complying with NPDES regulations and federal metal molding and casting effluent guidelines, several sludge samples from the impoundment were collected and analyzed. Several samples released lead in the EP Toxicity Test above the hazardous waste criterion of 5.0 mg/L.

Bench-scale treatability tests were conducted with various chemical additives to evaluate treatment possibilities for rendering the sludge non-EP Toxic. Results indicated that the lead

EP Toxicity concentration could be reduced to less than 2 mg/L using phosphoric acid at a dosage of approximately 2 gallons phosphoric acid per ton of dry solids (gpt). The bench-scale tests also showed that both the pH and the residual dissolved phosphate concentration of the wet sludge after treatment were good indicators of treatment effectiveness. This was important because EP Toxicity results require several days to obtain, whereas pH and dissolved phosphate results can be available in minutes. Based on these results, an in-line wastewater treatment system was designed and installed upstream of the impoundment to treat the incoming solids and prevent generation of new hazardous sludge.

After bench-scale testing, a process assessment was performed to evaluate several treatment options and to develop a conceptual design for the selected treatment system, based on technical, economic, and regulatory constraints. Because the impoundment was a critical part of the foundry's wastewater treatment system, the dredging and treatment were required to occur while continuously operating the surface impoundment. Based on the bench-scale treatability testing and process assessment, the selected treatment process included hydraulically dredging the impoundment sludge to an existing on-site landfill designed to handle dredged slurries. The sludge would be treated with in-line chemical treatment to render the
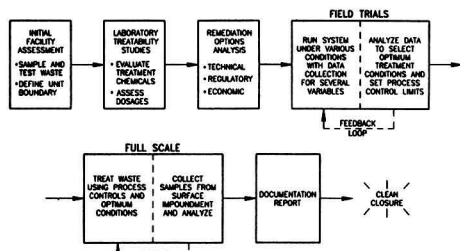
FIGURE 1. Remediation of a foundry surface impound-ment—project summary.

FIGURE 3. Conceptual treatment process flow sche-matic—surface impoundment sludge treatment.

solids non-EP Toxic. The treated solids would settle in the landfill and the supernatant would be returned to the impoundment. Detailed engineering was performed, the system was constructed, and field trials using full-scale equipment were run to demonstrate the ability of the treatment system. Based on the field trial results, modifications were made to the treatment system, and the impoundment was remediated by dredging and treating the sludge. Following dredging, a barge-mounted drill rig was used to collect samples in the impoundment and to document "clean closure."

This paper summarizes various aspects of the project (Figure 1), and focuses on the field trial and full-scale remediation portions.

BENCH-SCALE TREATABILITY TESTING

Several samples of the surface impoundment sludge, with initial lead EP Toxicity concentrations up to approximately 40 mg/L, were treated with different chemical additives to evaluate their ability to render the sludge non-EP Toxic. In part, the bench-scale treatability tests were designed to assess the following variables:
- Type and dosage of chemical additives.
- Final treated slurry pH.
- Concentration of solids in test slurry.

Significant treatment effectiveness was observed with the following additives:
- Magnesium hydroxide
- Triple superphosphate (TSP)
- Phosphoric acid

FIGURE 2. Reagent dosage vs. EP Toxicity.

TSP and phosphoric acid were effective in rendering the sludge non-EP Toxic at dosages significantly lower than magnesium hydroxide. Therefore, bench-scale treatability continued only with TSP and phosphoric acid. Figure 2 presents the results of the treatability tests with TSP and phosphoric acid.

The test results are summarized as follows:
- The lead EP Toxicity concentration of treated solids decreased sharply to approximately 2 mg/L with increasing phosphate dosage. To reduce the lead EP Toxicity to 2 mg/L, the required dosage was 1.5 percent by weight (dry basis) for phosphoric acid, compared to 2.5 percent by weight for TSP.
- Slurries treated with phosphoric acid contained slightly lower slurry pH and a higher residual dissolved phosphate concentration in comparison to slurries treated with TSP.
- For treated slurries with lower lead EP Toxicity, higher concentrations of residual dissolved phosphate were observed.

ASSESSMENT OF TREATMENT PROCESS ALTERNATIVES

Based on the bench-scale treatability results, phosphates were the most effective treatment additives. Therefore, several sludge treatment alternatives were evaluated for economic, technical, and regulatory considerations. Because the surface impoundment was a critical part of the foundry's wastewater treatment system and needed to remain in operation, hydraulic dredging was selected as the sludge removal method. The treatment alternatives included continuous in-line treatment of the hydraulically dredged slurry using the following phosphate additives:
- Phosphoric acid
- Slurried triple superphosphate
- Dry granular triple superphosphate

The treatment process assessment considered hydraulic dredging rate, chemical requirement, availability, delivery, ease of material handling, unit costs, and other factors. The sludge treatment process is conceptually shown on Figure 3. The treatment chemical would be delivered to the site in tank trucks and unloaded into storage tanks. The sludge would be dredged and conveyed via a pipeline to a reaction tank. Phosphate would be added to the dredged slurry upstream of the reaction tank, and would react with the solids prior to discharge in the on-site landfill. During field trials, the treated slurry would flow from the mixing tanks back to the impoundment. During full-scale operations, the treated slurry would be discharged to a state-approved, on-site, solid waste landfill designed with leachate and supernatant liquid collection systems. In the landfill, the treated solids would settle out, and supernatant water would be recycled back to the wastewater treatment system.

Based on preliminary cost estimates developed during this assessment, agricultural-grade phosphoric acid was determined
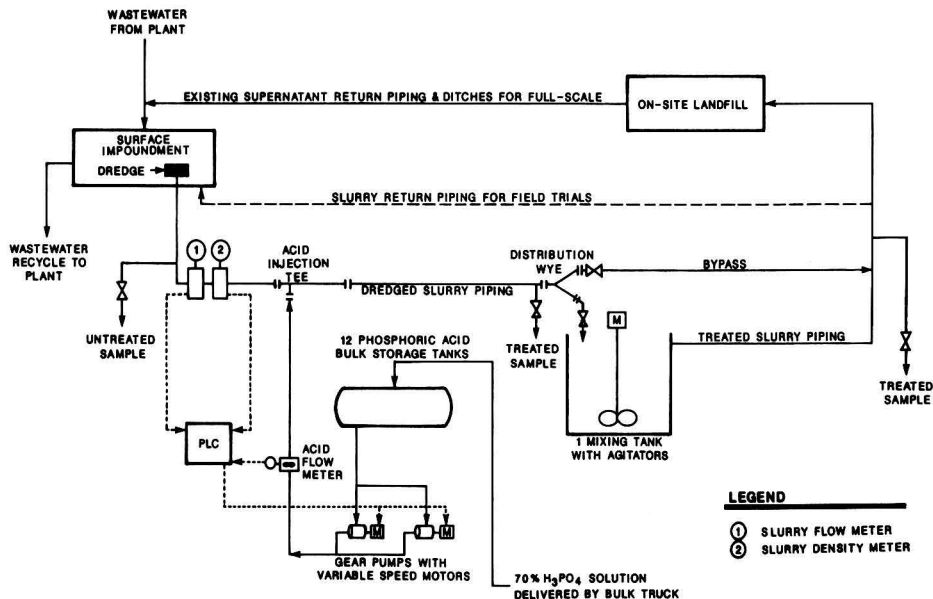
FIGURE 4. Treatment process flow schematic—modified system after field trials start-up.

to be the most cost-effective treatment additive. In comparison, the projected costs with technical-grade phosphoric acid and TSP (slurried or granular) were higher by approximately 30 percent and 50 percent, respectively. Agricultural grade phosphoric acid appeared more cost effective because of low dosage requirements and shorter project durations, due to anticipated ease of handling and a higher rate of sludge processing. Therefore, field trials used agricultural-grade phosphoric acid.

FIELD TRIALS

The major objectives of field trials were to demonstrate treatment effectiveness during continuous, full-scale operation and evaluate the performance of the treatment system using full-scale equipment. Determining operating conditions for full-scale remediation was another major objective.

The Planned Treatment Process

A schematic of the treatment system is shown on Figure 4. The major components include a hydraulic floating dredge plus a slurry pipeline—approximately 1 mile long. Phosphoric acid storage and feed pumps plus instrumentation and process controls for acid injection into slurry pipeline and mixing tanks were also major components.

Sludge would be dredged continuously and pumped through the pipeline. Agricultural-grade phosphoric acid, with a 70 percent concentration by weight, would be injected into the pipeline to render the solids non-hazardous. Chemical reaction would occur in the pipeline and in the mixing tank. During field trials, treated slurry would be discharged by gravity to the surface impoundment to eliminate any possible discharge of untreated or under-treated solids into the landfill area during this trial period.

To minimize the problems due to cold weather, the acid feed pumps, all instrumentation and controls, the acid injection tee, and the critical acid feed system piping were located indoors. All other piping, the acid storage tanks, and the acid mixing tanks were located outdoors. The acid concentration used (70%

by weight) was selected as the highest concentration with a freezing point above the anticipated temperatures. The layout of the dredge slurry pipeline was designed so that it would be primarily self-draining after a dredge shutdown. The mixing tanks were also designed to be drained.

A doppler slurry flow meter and a nuclear density meter would be used to continuously measure the mass flow rate of solids in the dredged slurry. Automatic control of the phosphoric acid feed rate would be provided to maintain a feed rate proportional to the mass flow rate of dry solids in the slurry. The remediation contractor provided a control system to control the phosphoric acid feed rate based on a programmable logic controller (PLC). This allowed the system controls to be developed and changes to be made to the controls by programming the PLC software via a microcomputer. It also allowed the use of a graphics monitor for control of the treatment system. The PLC and graphics monitor allowed the operator to view any of the several monitor screens to rapidly check the status of various parts of the treatment system, respond to system alarms, or adjust treatment system operation (including changing the system control mode, adjusting the system setpoint dosage, and starting or stopping the acid feed pumps) as desired.

To minimize corrosion by the acid, type 316 stainless steel was used for all pumps, piping, valves, and instrumentation in contact with H_3PO_4, and polyethylene was selected for the acid storage tanks. High-density polyethylene (HDPE) was selected for the 14-inch-diameter, 1-mile-long slurry pipeline.

Samples of the untreated slurry would be used for periodic calibration of the total suspended solids measurements of the density meter. Hourly measurements of pH and residual dissolved phosphate in the treated slurry would be used to obtain "real time" treatment effectiveness information. Samples of untreated slurry and treated slurry would also be collected hourly and tested for lead concentration using the EP Toxicity test to confirm the success of treatment. These results would also be used to develop correlations between EP Toxicity with pH and residual dissolved phosphate, so that they could be used as "real time" treatment effectiveness monitors.

To evaluate the relationship between acid dosage and EP Toxicity using full-scale treatment equipment, the phosphoric

Table 1 Treatment System Control Modes

Control Mode	Slurry Flow Meter	Slurry Density Meter	Comments
Automatic	In operation	In operation	Normal system mode of operation
Flow	In operation	Out of service	Set slurry solids concentration = 30%
Suspended solids	Out of service	In operation	Set slurry flow rate = 5,000 gal/min
Manual	Out of service	Out of service	Set slurry flow rate = 5,000 gal/min and slurry solids concentration = 30%

Table 2 Field Trials Plan

Field Trial Number	Objectives	System Control Mode	Acid Dosage (gal/ton)
1	• Start up and debug system equipment. • Calibrate system instrumentation and controls.	Manual	none
2	• Demonstrate system operation in the automatic control mode. • Evaluate treatment results at an acid dosage of 2.1 gal/ton.	Automatic	2.1
3	• Conduct additional field trials at dosages ranging from 1.5 to 4.1 gpt.	Automatic	variable

acid dosage rate was varied from approximately 1.5 to 4.1 gallons of 70 percent acid per ton of solids (gpt).

Field Trial Plan

A field trial plan was developed to systematically evaluate the following variables which were expected to significantly affect the treatment system's performance:
- Slurry flow rate (3,000 to 5,000 gpm was anticipated).
- Slurry solids concentrations (5% to 30% was anticipated).
- Acid dosage (1.5 to 4.1 gpt was anticipated).

In addition, field trials were designed to evaluate the following:
- Ability of instrumentation to accurately and precisely monitor process variables (slurry flow rate, slurry solids concentration, and acid flow rate).
- Ability of the controls to maintain the acid dosage within an established range of the set point dosage.
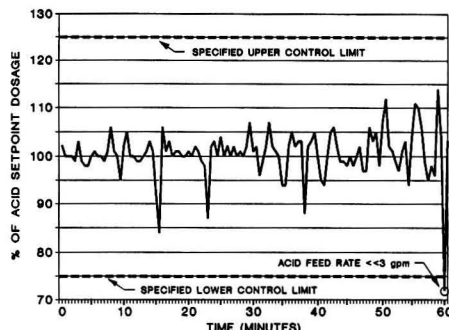
FIGURE 5. Actual vs. setpoint dosage for a one-hour period during field trials.

- Reliability of mechanical components (pumps, valves, mixing tanks, mixer).

Table 1 shows the field trial treatment system control modes. Because of the uncertainty concerning the accuracy, precision, and reliability of the treatment system components, the acid feed system was designed to operate in any of four control modes. By providing operating flexibility in the control system design, the reliability of the treatment system could be maintained during periods when one instrument was inoperable.

Table 2 summarizes the field trial plan. This plan was used to guide the field trial test runs, make decisions concerning additional test runs, and provide a basis for evaluating the success of field trials.

Field Trial Treatment System Performance

In general, the components, instruments, and controls of the treatment system performed satisfactorily during field trials. However, breakdowns and required maintenance of the hydraulic dredge and calibration of the slurry density and flow meters resulted in interruptions. The mixing tanks experienced considerable mechanical difficulties when rocks and large debris were encountered. A bypass was installed around the mixing tanks to overcome the problems with the mixing tanks, and field trials were run with and without the mixing tanks to determine the effect of the mixing tanks on treatment system performance. The concentration of solids in the dredged slurry varied considerably as the cutter head of the hydraulic dredge collected sludge. The approximate range of operating conditions for the treatment system during field trials was as follows:
- Dredge slurry flow rate = <2,700 to >4,000 gpm (4,000 gpm typical).
- Concentration of solids in slurry = <1 to >30% by weight (10 to 20 percent by weight typical).
- Solids mass flow = <0.5 to >10 tons per minute (1.5 to 6 tons per minute typical).
- Acid dosage rates = 1.5 to 4.1 gallons per ton.

Table 3 Treatability Testing Results From Field Trials

Acid Dosage (gal/ton)	Lead EP Toxicity Test Result		
	Number of Samples	Average (mg/L)	Maximum (mg/L)
0	37	7.2	36
1.5	9	1.0	4.1
2.1	10	0.6	1.3
2.5	9	0.1	0.2
3.1	3	0.3	0.5
3.6	8	0.4	1.4
4.1	4	0.1	0.1

Despite this wide range of operating conditions, the treatment system worked reliably after the initial start-up and debugging. This increased the confidence that the system would provide the reliability needed during the full-scale remediation. A key consideration in evaluating the field trial results was the ability of the control system to track variations in slurry mass flow rate and to maintain a sufficient acid feed rate to achieve the desired dosage (i.e., the setpoint dosage). Based on nearly 500 readings comparing actual versus setpoint dosage, the average actual dosage was 100.06 percent of the setpoint dosage, with a standard deviation of 8.70 percent when the acid feed rate was above 3 gpm.

Figure 5 shows a graph of the actual versus setpoint dosage during one of the field trial runs. This is typical of the setpoint control achieved during the other field trial runs after the controller had been adjusted to optimize setpoint control.

Field Trial Treatment Testing Results

The field trial treatment testing results showed that the lead EP Toxicity could be reduced to <2 mg/L at a phosphoric acid dosage of approximately 2.1 gpt. The field trial results at various dosages are shown in Table 3.

The field trial data were statistically evaluated to develop confidence intervals for EP Toxicity versus acid dosage. A log transformation of the parameter values were performed and fitted by a least squares linear regression. The difference between observed and predicted values (residuals) showed a normal distribution. Various confidence intervals were computed for acid dosages ranging from 0 to 4.5 gpt. This statistical evaluation showed that an acid dosage of approximately 2.1 gpt would provide a 99.9 percent confidence that the average lead EP Toxicity results would be below the action limit of 2.0 mg/L.

In addition to EP Toxicity, pH and residual dissolved phosphate analyses were performed on an hourly basis. The pH of the untreated and treated slurries ranged from approximately 8 to 9 and 6 to 7, respectively. Generally, treated slurry samples with lower pH values after treatment were associated with higher residual dissolved phosphate concentrations and with lower lead EP Toxicity concentrations. Unfortunately, residual dissolved phosphate data were highly variable, and were not correlated with the lead EP Toxicity data, unlike the observations during bench-scale treatability testing. It was believed that the in-field residual phosphate measurements may have been subject to greater analytical difficulties, due to field conditions. Therefore, a modified analytical procedure was recommended for full-scale. In any event, both pH and residual dissolved phosphate measurements provided a positive indication that acid was being injected into the slurry pipeline and that the sludge was undergoing treatment. Therefore, these parameters could at least be used as "real-time" monitors of general trends in treatment performance.

Based on the field trial results, the following major conclusions and recommendations were reached:

- Lead EP Toxicity decreased sharply at acid dosages up to approximately 2.0 gpt. At dosages above 2.0 gpt, little additional EP Toxicity reduction was observed. These results confirmed the observations on EP Toxicity reduction during bench-scale treatability testing discussed earlier.
- There was no significant difference in EP Toxicity concentrations of samples collected before the mixing tank, and samples collected after the mixing tank. Therefore, it was recommended that the mixing tanks be eliminated and replaced by additional slurry piping after the point of acid injection. The added pipe would provide equivalent reaction time as used in the field trial system.
- None of the treated solid samples showed lead EP Toxicity concentrations higher than the hazardous waste limit of 5.0 mg/L. Only one treated solids sample had a lead EP Toxicity concentration above 2.0 mg/L (at an acid dosage of 1.5 gpt), and no results were above 2.0 mg/L at higher dosages. Therefore, based on a statistical evaluation of the data, 2.0 gpt was recommended as the initial setpoint dosage for full-scale remediation.

The field trials using full-scale equipment demonstrated that the settling basin sludge could be effectively treated in continuous operation by injecting phosphoric acid into a dredged slurry pipeline, and determined the operating conditions for full-scale remediation.

FULL-SCALE REMEDIATION

After the recommended modifications were made to the treatment system, full-scale remediation began with 24 hours per day 6 days per week operation. During full-scale, operational items included the following:

- Operation in the "automatic" control mode whereby the acid injection rate was proportional to the mass flow rate of solids in the slurry.
- Hourly analysis of untreated slurry for pH.
- Hourly analysis of treated slurry for pH and residual dissolved phosphate.
- Hourly collection of treated slurry solids for preparing an 8-hour composite for EP Toxicity leaching.
- Implementation of "real time" process control to adjust the phosphoric acid dosage.

"Real Time" Process Control

Due to the importance of successfully treating all sludge to below the RCRA hazardous waste criterion of 5.0 mg/L for lead EP Toxicity, 2.0 mg/L was selected as the treatment "target" level. However, the EP Toxicity test required about 1 week to complete, and a significant quantity of untreated and under-treated sludge could be placed in the on-site landfill during that time. Therefore, "real time" process control was extremely important.

Based on the database of treated slurry pH, residual dis-

solved phosphate, and EP Toxicity results from field trials, statistical correlations between these parameters were developed. However, due to the variability of the data, limited success was realized. During full-scale, the database expanded and linear correlations were observed following log transformations of the residual dissolved phosphate and lead EP Toxicity results. Using the relationship between EP Toxicity and residual phosphate, and assuming a conditional distribution approximated by the t-distribution, a phosphate value which corresponded with a lead EP Toxicity value could be calculated for various confidence levels.

Initially, the phosphate value corresponding to 2 mg/L lead EP Toxicity and the 99 percent confidence level was chosen as the target "real time" level.

Using this residual dissolved phosphate target concentration and standard process control procedures, a CUSUM V-mask control system was developed, based on phosphate results in the treated slurry. The control system tracked deviations of phosphate concentrations from the target value, in order to establish long-term tendencies. When the tendencies became statistically significant, other technical qualitative factors were considered, and the dosage rate was adjusted.

The system was operated successfully for approximately 1 month with the target residual dissolved phosphate concentration determined by the 99 percent confidence of attaining 2 mg/L lead EP Toxicity. The target phosphate concentration was then revised to equal the 99-percent confidence of attaining 4 mg/L lead EP Toxicity, and the treatment system was operated for approximately 5 months to complete the initial remediation of the surface impoundment. Over 300,000 cubic yards of material were successfully dredged and treated during this time.

Full-Scale Remediation Results

Over 200 composite treated solids samples were analyzed by the EP Toxicity test for lead. The average lead EP Toxicity concentration for these samples was approximately 0.5 mg/L, with approximately 98 percent of the values below the hazardous waste limit of 5.0 mg/L.

Duplicate samples were analyzed for the remaining 2 percent of the composite samples with lead EP Toxicity exceeding 5.0

mg/L. All of the duplicate samples had lower lead EP Toxicity and residual dissolved phosphate concentrations than the concentrations of the initial samples, indicating that the reaction of lead and phosphate continued without the agitation that was present in the pipeline. In fact, with the duplicate sample results, none of the reanalyzed (releached) treated slurry samples exceeded the RCRA EP Toxicity criterion for lead.

CLEAN CLOSURE DEMONSTRATION

After successfully dredging and treating over 300,000 cubic yards of sludge, samples of the material remaining in the impoundment were sampled and analyzed. These remaining materials consisted of underlying clay, recently deposited wastewater sludge, and foundry sand. The RCRA clean closure performance standards required that the sludge be tested for lead EP Toxicity and compared to the RCRA EP Toxicity criterion for lead, and that the other materials be tested for compositional metal concentrations and compared to background concentrations.

Approximately 300 samples from the bottom of the impoundment were analyzed to document that the impoundment met the RCRA clean closure performance standards. Samples were collected using a barge-mounted drill rig, and tested for EP Toxicity and total (compositional) metals. The results indicated that the sludge had not significantly impacted the underlying soil, based on a statistical comparison of metals concentrations between background soil and underlying soil. The results also indicated that the clean closure performance standards for removing EP-Toxic sludge had been satisfied.

CONCLUSION

A continuous process, where phosphoric acid was injected into a dredged slurry for treatment of EP-Toxic sludge, was successfully implemented to remediate over 300,000 cubic yards of sludge in a foundry surface impoundment while the impoundment and the foundry production processes remained in operation.

Application of Amines for Treating Flue Gas From Coal-Fired Power Plants

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Some of the earliest applications of amines for treating flue gas were to recover carbon dioxide for dry ice production and beverage carbonation. The amine process was later applied to recover CO_2 for urea production. In the late 1970's and early 1980's during the period of major enhanced oil recovery projects, amines were used to recover CO_2 from flue gas for injection. In those plants, SO_2 was typically removed by an alkaline scrubbing system upstream of the amine process, but nothing was done to reduce the NO_x and excess oxygen in the flue gas. Residual SO_2, NO_x, and oxygen caused amine degradation and in some cases led to severe corrosion.

Recent advances have been made in hydrotreating of power plant boiler flue gases to reduce SO_x and NO_x, the major components of acid rain, to hydrogen sulfide and nitrogen, and to convert excess oxygen to water. The sulfur pollutants in the form of H_2S can be recovered and converted to elemental sulfur by a selective amine unit and a Recycle Selectox sulfur recovery unit. This combination of units, the Parsons Flue Gas Cleanup (FGC) Process, shows great promise in abating the SO_x and NO_x pollutants from coal-fired power plants and provides a novel use for selective amines.

This paper reviews some of the earlier applications of amine in flue gas treating and the recent development of the Parsons FGC Process for over 99 percent removal of both SO_x and NO_x.

BACKGROUND

Applications of amines for treating coal-fired boiler or power plant flue gas have long been an important process step in carbon dioxide recovery. Beginning in the late 1930's monoethanolamine (MEA) was used to recover CO_2 from coal or coke-fired power boilers flue gas [1]. The recovered CO_2 was then compressed, cooled, dried, purified and expanded to produce liquid CO_2 or dry ice for refrigeration. This market is the largest nonoil field use of CO_2. The second largest non-oil field market use of CO_2 is for beverage carbonation.

Ammonia plants have been the traditional industrial sources for by-product CO_2 [2]. Urea production is mostly based on the supplies of by-product CO_2 from ammonia processes, but supplemental CO_2 is required when all the ammonia is being converted to urea. The MEA process has been applied more recently to recover additional CO_2 from reformer flue gas to increase urea production. This market still looks promising in the developing countries but not in the generally weak U.S. fertilizer sector.

Another important application of amines to recover CO_2 from flue gas that developed during the late 1970's and early
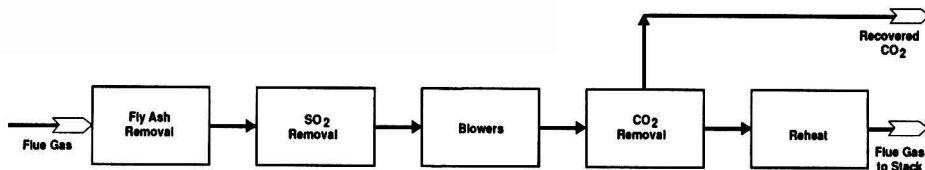
FIGURE 1. Block flow diagram CO_2 recovery from flue gas.

1980's period was for enhanced oil recovery (EOR). Enhanced oil recovery using CO_2 represents the largest single market potential for amine applications, even though the current low oil prices do not provide the economic incentives for any new CO_2 injection project.

Parsons has designed and constructed two MEA plants which remove large quantities of CO_2 from flue gas for use in chemical processing. The first plant built for ITT Rayonier at Hoquiam, Washington recovers 80 short tons of CO_2 from a boiler flue gas generated by the combustion of fuel oil [3]. The second plant built for Kerr-McGee at Trona, California recovers CO_2 from a flue gas generated by the combustion of a mixture of Western coal and high sulfur petroleum coke in a pair of 600,000 lbs/hr, 1500 psi steam boilers [4]. The plant was designed to recover 630 short tons of CO_2 in two parallel trains.

CO_2 RECOVERY PROCESS SCHEMES

Flue gas generated from the combustion of low cost fuel such as coal is at near atmospheric pressure and contains contaminants such as fly ash particulates, sulfur oxides and nitrogen oxides. Figure 1 is a typical block flow diagram of a plant which recovers CO_2 from flue gas generated by a coal-fired boiler. Recovery of CO_2 from low pressure and oxygen containing coal-fired boiler flue gas presents some unique problems when compared to other gas treating applications.

Fly Ash Removal

A typical flue gas stream from a coal-fired boiler contains 2 to 4 grains/SCF of fly ash particulates. Fly ash in the flue gas can cause plugging, foaming, erosion/corrosion and solvent degradation problems in the CO_2 recovery system. These particulates must be removed from the flue gas by either an electrostatic precipitator (ESP) or bag-house. A 99.8 percent efficient ESP or bag-house will lower the fly ash loading to less than 0.01 grains/SCF.

Oxygen

A coal-fired boiler is typically operated with 20% excess air and will have a flue gas containing approximately 3.5% oxygen. The presence of oxygen can lead to amine degradation and severe corrosion problems. Use of an inhibited amine system (6, 7) or exotic alloys are generally required to cope with the oxygen problem.

Sulfur Oxides

As opposed to many gas treating operations where sulfur is present primarily as H_2S, the sulfur in boiler flue gases is primarily SO_2 with traces of SO_3. Combustion of typical high
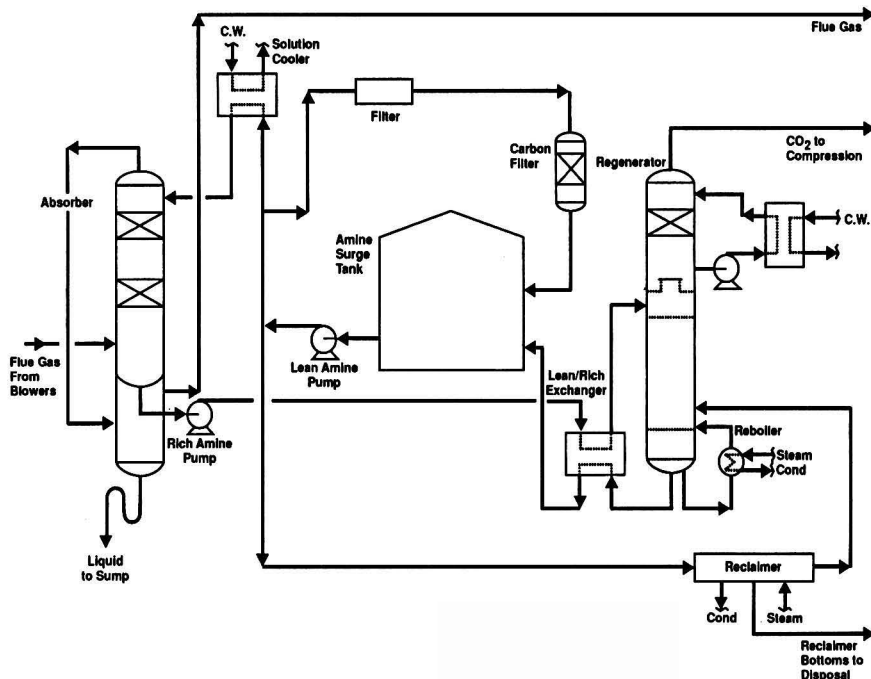
FIGURE 2. Process flow diagram CO_2 removal plant.
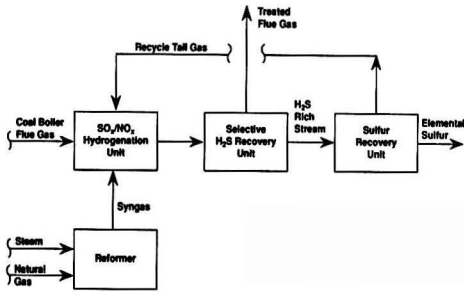
FIGURE 3. Parsons FGC Process block flow diagram.

sulfur coal containing 4% (wt.) sulfur results in approximately 0.35% (vol.) SO_2 in the flue gas [8].

Conventional flue gas desulfurization (FGD) systems such as the most widely used wet limestone and wet lime processes with a typical removal efficiency of 90 to 95% will bring the outlet SO_2 concentration down to 100–200 ppmv depending on the feed concentration. Each mol of SO_2 in flue gas will neutralize two mols of MEA solvent. The presence of SO_x in flue gas will lead to heat stable salts formation, solvent degradation, and a substantial increase in reclaiming requirements. This can result in excessive amine solvent losses and severe corrosion problems. It is very important to remove sulfur oxides to the lowest possible level before the flue gas enters the CO_2 recovery process.

Nitrogen Oxides

The NO_x present in flue gases affects amine systems in a manner similar to oxygen. It has been reported that one CO_2 recovery plant required the removal of all oxygen and NO_x to less than 1 ppm in the flue gas prior to the MEA contactor [9]. The presence of NO_x led to severe corrosion attack at the bottom of the contactor. Some of the possible NO_x control schemes are low NO_x burner and Selective Catalytic Reduction (SCR).

Carbon Dioxide Removal

The monoethanolamine (MEA) process has been the most extensively used process for treating flue gases to recover CO_2.

Flue gases from coal-fired boilers are available at near atmospheric pressure with typical CO_2 concentration of 13 to 16%. The low CO_2 partial pressure favors stronger alkalies such as MEA. The MEA process can easily remove more than 90% of the CO_2 in flue gas at relatively low pressure. MEA also has the lowest boiling point of the conventional amines and consequently is the easiest to separate from dissolved salts and degradation products by semicontinuous batch distillation or reclaiming. Figure 2 is a process flow diagram of a typical MEA CO_2 removal plant. In the presence of oxygen and NO_x, MEA with no inhibitor is generally run at concentrations between 10 and 15 percent to avoid any severe corrosion problems and to simplify reclaiming. MEA with added inhibitor can be run at concentrations up to 25 to 30 weight percent.

INNOVATIVE APPLICATION OF AMINES FOR FLUE GAS CLEANUP

In July 1989, the Bush administration proposed a comprehensive draft of the Clean Air Act aimed at reducing emissions of SO_x and NO_x, implicated in acid rain and urban smog formation as well as emissions of a wide range of toxic air pollutants [10, 11]. The proposal advocates reducing utility SO_2 emissions by 10 million tons from the 1980 level by the year 2000. It also proposes a reduction of NO_x emissions by 2 million tons from the projected 2000 level. When the program is complete, Electric Power Research Institute (EPRI) estimates that the SO_2 control cost to utilities will be about $4 to $6 billion per year. Adding NO_x control, the total could reach $5 to $8 billion per year.

As one can see from the previous examples, existing applications of amines to treating coal-fired boiler flue gas have been limited only to CO_2 recovery. In the past, contaminants in flue gas were removed by scrubbing methods as outlined above. Now, these contaminants can be removed by a novel technology involving hydrogenation of the SO_x, NO_x, and O_2. The sulfur pollutants are converted to an amine removable form (H_2S) in the hydrogenator. Other amine contaminants such as NO_x and Oxygen are converted to harmless N_2 and H_2O prior to the amine unit. Therefore, these new advances in technology expand the use of amines from CO_2 recovery to flue gas cleanup. The hydrogenation step produces no waste stream as opposed to the sludge or slurry produced by the conventional FGD units.

The Ralph M. Parsons Company and a consortium of co-sponsors have developed the Parsons Flue Gas Cleanup (FGC)
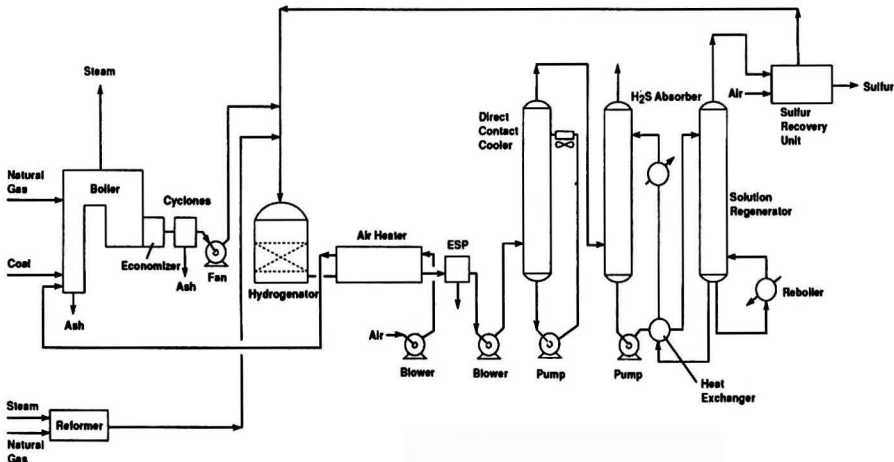

FIGURE 4. Parsons Flue Gas Cleanup Process.

Process to remove 99+ percent of both SO_x and NO_x from coal-fired boiler flue gases. This process includes the use of the selective amines for removing the sulfur pollutants in the flue gas. The description, technology and development of the Parsons FGC Process are presented in the following sections.

PROCESS DESCRIPTION

The Parsons FGC Process includes the following steps:
- Simultaneous catalytic reduction of sulfur oxides (SO_x) to hydrogen sulfide (H_2S), and nitrogen oxides (NO_x) to nitrogen (N_2) in a hydrogenation reactor.
- Recovery of H_2S selectively in the presence of significant amount of CO_2 from the hydrogenation reactor effluent gas.
- Production of elemental sulfur from H_2S-rich gas.

A process block flow diagram and a process flow sketch for a sample Parsons FGC plant are presented in Figures 3 and 4. Flue gas feed to the FGC plant is removed after the boiler's economizer and passed through a multicyclone assembly where large ash particles are removed. The resulting flue gas is then mixed at an elevated temperature with steam-methane reformer gas and downstream sulfur plant recycle tail gas to form the feed to the catalytic hydrogenator where O_2, SO_x, and NO_x reductions occur. The proprietary catalyst uses a ceramic honeycomb substrate that permits passage of flue gas particulates with low pressure drop.

The hot hydrogenator effluent is used to preheat the boiler combustion air in a low leakage air preheater. The ash remaining in the flue gas is then removed in an electrostatic precipitator and the cleaned flue gas is fed to a desuperheater/contact condenser. Here, the gas is cooled and moisture is removed by condensation. Water condensed from the flue gas is steam-stripped to remove H_2S so that it can be recycled as high quality condensate for use in the plant. A blowdown stream from the desuperheater/condenser is filtered and sewered.

The effluent flue gas from the contact condenser enters an absorption column where it is contacted with an H_2S-selective solvent. Two of the preferred selective amines are FLEXSORB SE PLUS licensed by Exxon and Union Carbide's UCARSOL HS-103 solvent. Essentially, all of the H_2S and a small portion of the CO_2 in the flue gas is absorbed by the solvent. The absorber effluent gas containing less than 10 ppmv H_2S, an environmentally acceptable level, is then vented to the atmosphere.

The H_2S-enriched solution leaves the bottom of the absorber and enters the regenerator, where it is heated and steam-stripped to release the acid gases from solution. The H_2S-containing offgas exiting the top of the regenerator is sent to a Recycle Selectox sulfur plant that converts the H_2S to elemental sulfur. The Recycle Selectox process is licensed jointly by Parsons and Unocal.

The salable, bright yellow elemental sulfur is collected as a liquid product and the tail gas is recycled to the hydrogenation reactor for further sulfur recovery.

PROCESS TECHNOLOGY

The Parsons FGC Process consists of three key process units, each of which has been proven in commercial applications but applied it the first time for coal-fired boiler flue gas.

$$SO_x - NO_x - O_2 \text{ Hydrogenation}$$

Simultaneous catalytic reduction of SO_2 and NO_x has been practiced commercially for years by Parsons in its Beavon Sulfur Removal (BSR) process units. The BSR Process was developed jointly by Parsons and Unocal in the early 1970's. Seventy BSR plants have demonstrated the commercial reliability of the hydrogenation, H_2S recovery, and sulfur production steps in tail gas plants treating feed gases containing approximately 10,000 ppmv of sulfur compounds consisting of SO_2 and H_2S. Extension of this experience to FGC operations requires the ability to process flue gas with the more dilute feed concentrations (from 2,000 to 3,500 ppmv of SO_2) in the presence of fly ash particulates and any residual O_2 in flue gas.

This objective is being achieved by use of a honeycomb catalyst substrate and development of proprietary active catalyst ingredients to achieve the FGC process objectives. Highly favorable chemical thermodynamic equilibrium encourages essentially complete reduction of SO_x, NO_x, and O_2 at a 700°F (371°C) reaction temperature. An effective catalyst system will, therefore, result in essentially quantitative $SO_x - NO_x - O_2$ reduction.

H_2S Recovery by Selective Amine

The success in deploying an amine system for flue gas cleanup depends on the conversions of essentially all the SO_x, NO_x, and O_2 (the major components in flue gas causing solvent degradation and severe corrosion) to selectively removable H_2S and harmless N_2 and H_2O. Complete removal of SO_x, NO_x, and O_2 in the BSR hydrogenation unit ensures smooth and trouble-free operation at the selective amine unit. It also minimizes any reclaiming requirements and solvent make-up. The hydrotreated flue gas to the amine absorber with 2,000 to 3,500 ppmv of H_2S will have a typical CO_2/H_2S molar ratio range of approximately 40 to more than 80. The preferred amine system should be able to selectively remove the H_2S in the hydrotreated flue gas to a level of less than 10 ppmv at the following process conditions:
- Typical H_2S partial pressure of 0.03 to 0.06 psig (207 to 414 Pascal) at absorber inlet.
- Typical CO_2/H_2S molar ratio of 40 to more than 80.
- Maximum CO_2 slip through the absorber (at least 90% of the feed CO_2).

Two of the possible selective amine systems that can meet the process objectives are Exxon's FLEXSORB SE PLUS hindered amine and Union Carbide's UCARSOL HS-103 solvent. There are now about 13 UCARSOL HS-103 solvent units treating hydrogenated sulfur plant tail gases to less than 10 ppm H_2S. The CO_2 slip from these HS-103 units is typically about 90 percent. In the case of FLEXSORB SE PLUS amine system, more than 95% CO_2 slip can be achieved. This maximum CO_2 slip minimizes the reboiler duty requirements. There are 18 commercial FLEXSORB plants, five of them being FLEXSORB SE PLUS systems. The regenerated amine solvent
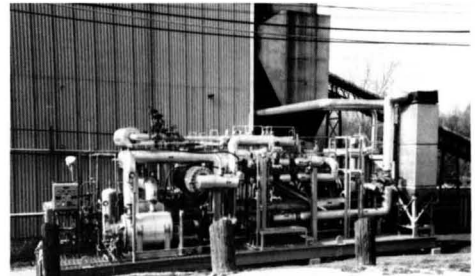

FIGURE 5. Pilot plant installed at St. Marys, Ohio.

produces an acid gas that is still rich in carbon dioxide and lean in hydrogen sulfide but one that is an ideal acid gas feed for a Recycle Selectox unit.

Sulfur Production

The Recycle Selectox process is the preferred choice to produce salable elemental sulfur from the H_2S-rich gas stream produced by the selective amine H_2S recovery system. The Recycle Selectox process was developed by The Ralph M. Parsons Company and Union Oil Company of California in the early 1980's. It was designed specifically to produce elemental sulfur from dilute H_2S gas feed streams. Twelve commercial plants have proven its viability. An overall review of the Selectox process can be found in a paper presented by Gowdy and Delaney [12].

PROCESS DEVELOPMENT

The development of the Parsons FGC Process has included both the bench scale and pilot scale programs [13]. Because the H_2S recovery via selective amine and Recycle Selectox sulfur production technologies are both commercially proven, the objective of the development project was to confirm the applicability of the BSR hydrogenation process in treating coal-fired boiler flue gas.

Bench Scale

The primary objective of the bench scale work was to develop a catalyst system and to establish reaction conditions to meet the targeted 99 + percent removal of SO_x and NO_x in flue gas. The bench scale test results to date have experimentally confirmed the ability to prepare and use honeycomb substrate catalysts capable of reducing SO_x and NO_x by greater than 99 percent. Also, the catalyst systems are able to completely reduce any residual oxygen containing in the gas mixture to water.

Pilot Scale

The performance of the catalytic hydrogenation reactor has been tested in a pilot plant designed to process a 10,000 SCFH, maximum, flue gas slipstream from boiler No. 6 of the St. Marys Municipal Power Plant located in St. Marys, Ohio. Figure 5 is a photograph of the pilot plant installed at the St. Marys Municipal Power Plant.

In 1989, three proprietary catalyst systems were investigated at the site for a five-week period. Due to instrumentation and equipment design problems, only 90 + percent SO_x and 85 + percent NO_x conversions were obtained.

The pilot plant design has been modified in 1990. The modifications are aimed at improving equipment and instrument performance, and system reaction kinetics. Four proprietary catalyst systems were investigated for a two-month period. The pilot plant was operated 24 hours a day, 7 days a week. The

1990 pilot plant results produced consistent 99 + percent conversion for SO_x and 92 to 96 percent conversion for NO_x for two of the four tested catalyst systems.

CONCLUSION

Based upon the successful demonstration of the $SO_x - NO_x - O_2$ hydrogenation unit, a selective amine system can be adopted as one of the three key process units of the Parsons FGC Process in abating the sulfur pollutants (in the form of H_2S) from coal-fired power plants. These technological advances expand the use of amines in treating flue gas and provide a novel use for the selective amines in combating acid rain.

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Regeneration of Waste Chemicals from Liquid Redox Processes

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To avoid the increasingly costly disposal of the waste stream (blowdown) from liquid redox processes used to clean hydrogen sulfide from gases, a reductive burning recovery (RBR) process has been developed. Its initial installation has recently been completed at Dofasco Steel Inc., Hamilton, Ontario, in order to treat the effluent from two Stretford liquid redox systems.

The RBR system concentrates spent Stretford chemicals which are primarily sodium thiosulfate and sodiuim sulfate. The spent chemicals are then thermally destroyed in a reactor. The regenerated salts flow from the bottom of the reactor as a molten smelt containing sodium carbonate, sodium sulfide and sodium vanadate.

The molten salt stream is dissolved in water to form a regenerated solution which is fed back into the Stretford process. For the special case of coke oven gas cleaning, elemental sulfur is added to a portion of the regnerated solution in order to clean hydrogen cyanide from the coke gas before the gas is scrubbed with Stretford solution to remove hydrogen sulfide. The sodium thiocyanate product of hydrogen cyanide scrubbing is also thermally destroyed and regenerated by the RBR process.

RBR Technology essentially closes the Stretford process for cleaning coke oven and other industrial gases. Only a small amount of ash which has been filtered from the regenerated chemicals needs disposal.

INTRODUCTION

The Stretford liquid redox process is one of the best systems for hydrogen sulfide (H_2S) removal from gases, with greater than 99% removal efficiencies (Figure 1). However, a drawback to this system is the accumulation of three waste chemicals which inhibit the activity of the scrubbing liquor. Two of the problem chemicals formed via side reactions are sodium thiosulfate ($Na_2S_2O_3$) and sodium sulfate (Na_2SO_4). Also in the case of coke oven gas, HCN is present, which reacts to form sodium thiocyanate (NaSCN). These salts act as a deadload in the Stretford process. If a blowdown stream is not taken when the combined concentration of salts reach 300–400 grams per liter, the scrubbing of H_2S will become ineffective.

There has been no accepted means for disposal or regeneration of the spent Stretford chemicals. Traditionally, this effluent has been deepwelled, landfilled, or sent to an industrial waste company. However, this can become quite costly with
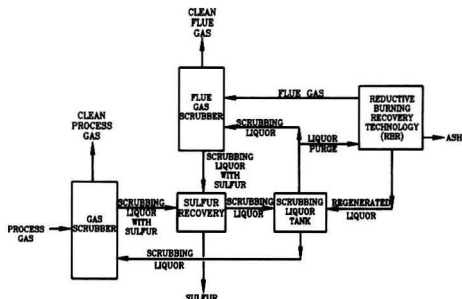
FIGURE 1. Stretford process.

FIGURE 2. Reductive burning recovery (RBR) process.

prices in the range of $0.50 to $1.00 per U.S. gallon [1]. Engineered Systems International has developed a cost effective system for the regeneration of the spent scrubbing chemicals, which essentially closes the Stretford process [2]. Only a small amount of ash filtered from the regenerated chemicals needs disposal. The system, call the Reductive Burning Recovery (RBR) process, uses thermal destruction to regenerate the blowdown stream. The prototype RBR is now operating at Dofasco Steel Inc. in Hamilton, Ontario, Canada, to treat both Stretford and HCN blowdowns.

RBR CHEMISTRY

The RBR system relies on high temperatures (greater than 1000°C) in the reactor to drive three key reactions. The first of these reactions involves the decomposition of NaSCN which proceeds as follows:

$$2NaSCN + 4H_2O \rightarrow Na_2CO_3 + 2H_2S + 2H_2 + CO + N_2 \quad (1)$$
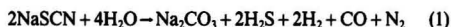
The next reaction involves the decomposition of sodium thiosulfate, which produces sodium sulfate and sodium sulfide [3].

$$Na_2S_2O_3 + Na_2CO_3 \rightarrow Na_2SO_4 + Na_2S + CO_2 \quad (2)$$

The sodium sulfate must be further reduced to sodium sulfide in the final reaction. This reduction can be done with efficiencies of greater than 80% when the sodium sulfate is in intimate contact with carbon on a hot char bed.

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2 \quad (3)$$
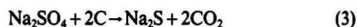
The end products of sodium sulfide and sodium carbonate flow from the bottom of the reactor in a molten state. These salts are dissolved in water and recycled back to the Stretford process and the HCN scrubber.

Analyses of the regenerated salts flowing from the reactor show that the decompositions of the NaSCN and $Na_2S_2O_3$ are greater than 90 percent. The decomposition of Na_2SO_4 is greater than 80 percent.

RBR PROCESS

The RBR process is a technology transfer from the chemical recovery process commonly found in kraft pulp and paper
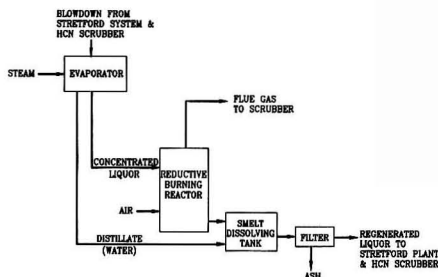
mills around the world. A simplified flow sheet of the RBR process is shown in Figure 2. The initial unit operation in the process is an evaporator, which concentrates the spent liquor from 20% total dissolved solids to approximately 65% solids. In the prototype installation, a two effect forced circulation evaporator was selected to minimize fouling and scaling. The concentration of the final product is controlled using the boiling point rise of the liquor.

The concentrated liquor from the evaporator is mixed with a carbonaceous fuel and sent into the reactor where reactions (1), (2), and (3) occur. Temperatures in the reactor are greater than 1000°C. A molten smelt flows from the bottom of the reactor.

The smelt flowing from the reactor is dispersed and dissolved with water produced in the evaporator system, and the resultant liquor is then sent to a filter press to remove suspended ash and any excess carbon. The filtered liquor is then returned to the Stretford process and HCN scrubber for reuse. The reactor flue gas is sent to a scrubber supplied with Stretford liquor to remove the H_2S before the gas is sent to the atmosphere.

Filter press operation is designed to wash the filter cake of soluble salts, which are returned to the smelt dissolving tank. The filter cake is then air dried to greater than 50 percent solids prior to dumping the washed cake containing mostly ash to landfill.

CONCLUSIONS

The reductive burning recovery (RBR) process essentially closes the Stretford liquid redox process for cleaning coke oven gas and other industrial gases containing H_2S. The waste sodium base chemicals from both Stretford and HCN scrubbing are thermally destroyed and regenerated in the RBR reactor. Waste chemicals which were once sent to disposal are now recovered and converted to usable salts to clean gas streams.

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Selection of Treatment Process to Meet OCPSF Limitations

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Allied-Signal manufactures phenol, a precursor for nylon 6, at its plant in Philadelphia, Pennsylvania. During this process wastewater is generated which is discharged to a POTW (Publicly Owned Treatment Works). The wastewater discharged has to meet the Organic Chemicals, Plastics, and Synthetic Fibers (OCPSF) pretreatment standard as defined in the U.S. EPA regulation 40 CFR 414.

In order to reduce concentrations of the various waste products, several technologies were evaluated including biological treatment, UV oxidation, and air stripping. Air stripping (or desorption) was initially rejected because it could not remove phenol to the desired level. Phenol has a low volatility which makes it difficult to strip. During the regulatory process, phenol was remanded from the list of OCPSF regulated chemicals. Therefore, air stripping was reevaluated as a treatment alternative. Additional studies showed that air stripping was the most cost effective method for removal of the regulated chemicals as well as a large percentage of the other volatile constituents. A thermal oxidizer was selected to destroy the organic compounds in the vapor stream from the air stripper column.

Pilot studies were conducted to confirm literature values for the mass transfer coefficients of the components. The pilot data were then used to size the full scale stripper.

The thermal oxidizer was designed using previous experience with handling similar compounds. Because of the high flow rates, heat recovery was added to minimize fuel costs. The equipment selection was based on cost effectiveness.

The paper will discuss the various issues encountered during the selection of the treatment process.

BACKGROUND

Allied-Signal's Frankford Plant located in Philadelphia, PA. manufactures phenol from the raw material cumene. A major by-product of this operation is acetone with a lesser amount of alpha-methyl styrene (AMS). The phenol produced is used in subsequent production processes to produce caprolactam, the monomer for nylon-6.

During the production process wastewater is generated from three primary sources. First, residual process air used for oxidation of the cumene is treated in charcoal adsorbers prior to release to the atmosphere. The adsorber beds are then regenerated with steam resulting in waste condensate. Second, wastewater is generated from steam used to strip high boilers in the acetone refining process. The remaining source for wastewater is the bottoms stream from a dephenolizer column used to strip phenol from water from various sources. These include vacuum ejector systems in the process area, leaks, and rain water run-off in the process area.

New regulations promulgated by the United States Environmental Protection Agency (USEPA) in 1987 for Organic Chemicals, Plastics and Synthetic Fibers (OCPSF) producers established limits for various compounds contained in

wastewater from these sources. Under these regulations pre-treatment is required even if the effluent water is discharged to a POTW which has the capability of removing the contaminants down to the treatment standard.

Of the originally regulated chemicals the plant effluent water contains only phenol at an average level 100 milligrams per liter (mg/L) and benzene at a level of 300 micrograms per liter (ug/L). The OCPSF regulations would have required a treatment level of 19 ug/L for phenol. However, phenol was remanded from the list of regulated chemicals in October 1989. The treatment standard for benzene remains in effect and requires treatment to a level of 57 ug/L on a monthly average.

The relatively small amount of benzene (less than one pound per day) which eventually is removed in the wastewater results from a trace amount found in the incoming raw material cumene. This benzene is trapped in the charcoal adsorber system and recovered with the steam condensate after regeneration. Benzene is typically not detected in the other wastewater streams.

From the regulatory standpoint one of the concerns and a primary motivation for the regulations is to minimize the impact of industrial wastewater on POTW facilities. Since phenol is not very volatile, it does not escape prior to treatment with the biological processes employed at the POTW. Also, these facilities derive a portion of their operating revenue from fees for treatment of this waste based on BOD content.

The stream containing the benzene amounts to approximately 30% of the total average plant effluent. The other streams contain a large amount of acetone which is unregulated but adds to the effluent BOD amount and hence, the surcharge for treatment. The effluent concentration of acetone of 2000 mg/L also has a significant effect on the design and cost (capital and operating) of the treatment process. Although only one of the three primary sources for wastewater contains benzene, it was decided that all streams would be treated to result in the lowest concentration of contaminants in the discharge to the POTW.

Prior to the remand of phenol from the regulated list of chemicals, the technologies evaluated were somewhat elaborate and expensive. This was because of the difficulty in removing phenol to the very low levels in the original treatment standards. These technologies generally have the capability of easily removing the small amount of the regulated chemical benzene as well as a large amount of the nonregulated constituents—acetone, AMS, and cumene.

TECHNOLOGY EVALUATION

Some of the technologies that were evaluated included:
1. Activated Sludge Treatment
2. Immobilize Cell Bioprocess
3. Granular Activated Carbon Treatment (GAC)
4. Powdered Activated Charcoal Treatment (PACT)
5. Ultraviolet Light Oxidation
6. Chemical Oxidation
7. Steam and Air Stripping

Air stripping was tested and initially rejected because of its inability to remove phenol. Once phenol was remanded from the list of chemicals, air stripping was reevaluated and proved effective in removing the regulated chemical benzene as well as a large percentage of the unregulated chemicals. Additional details on air stripping will be discussed below.

Activated sludge employs biological media suspended in clumps in a tank containing the wastewater. Air and nitrogen are added to the system to maintain proper growth and reproduction of the bacteria. Testing with this system was terminated because of unsatisfactory performance in removing phenol.

The immobilized cell bioprocess (ICB) is an emerging technology innovation under development by Allied-Signal. This process offers the advantage of maximizing biological action resulting in a compact system design. The process uses a unique media and a proprietary reactor design to enhance contact between the biofilm and the contaminants. The use of this technology may become significant for the removal of compounds that cannot be air stripped.

The granular activated carbon treatment facility uses a traditional charcoal adsorber process to treat the liquid stream. This process was studied at both the bench and pilot scale. Additional studies were performed to determine the operating and capital cost of a commercial scale system. These studies determined that this technology was highly variable in performance especially at high organic loading. In addition significant operating expenses would be incurred for replacement charcoal.

To treat the entire effluent flow of 360,000 gal./day (1360 m³/day) required approximately 12,000 lb./day (5440 kg/day) of carbon at a cost of $4.7 million annually. A primary reason for the high consumption rate is the large amount of acetone in the waste stream which limits the adsorption levels
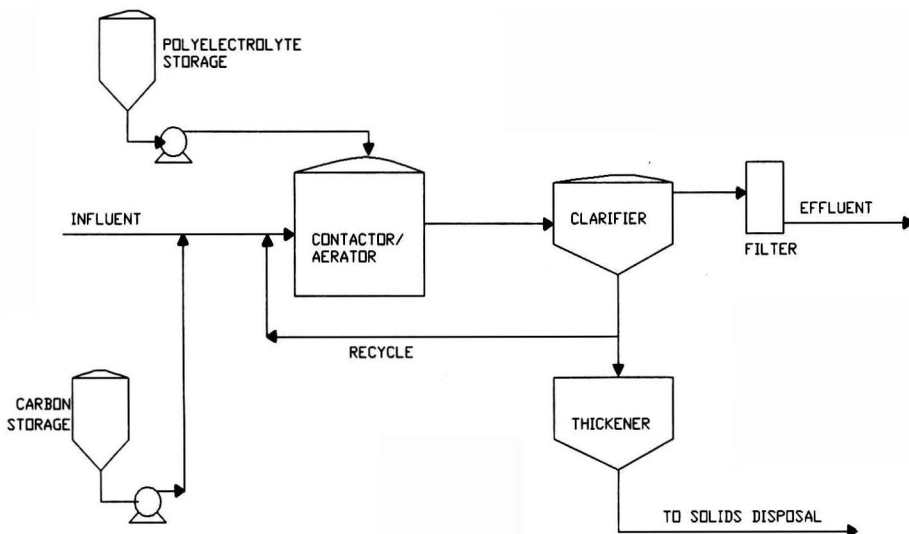

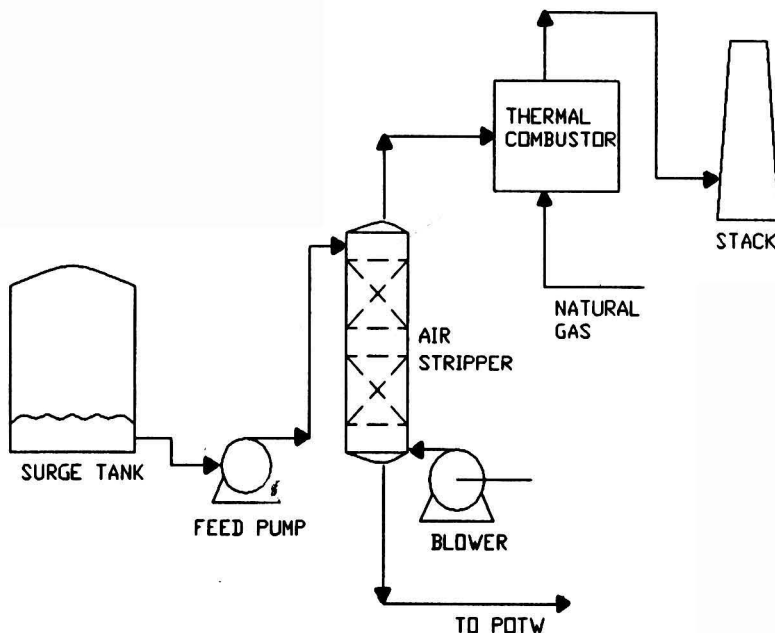**FIGURE 1. Typical PACT system flowsheet.**

FIGURE 2. Air stripping system.

of the regulated constituents. Steam stripping was evaluated to remove the acetone prior to treatment but did not prove viable because of the amount of acetone involved.

The PACT* system is a commercially available process for the treatment of wastewater containing a variety of priority pollutants. This system combines the features of the activated sludge system with those of an activated carbon system resulting in an enhanced treatment process. A typical flowsheet for this process is shown in Figure 1. The process involves the introduction of biological sludge media and the powdered activated carbon in a common addition tank. This tank is aerated and provided with sufficient residence time to affect the biological oxidation. The mixture from the contactor/aerator tank is sent to a clarifier where separation of powdered carbon and biological solids occurs.

The settled solids from the clarifier are returned to the contactor to maintain the concentration of biological and activated carbon solids.

A certain amount of fresh carbon and biological solids is added to replenish what is lost and to maintain the desired treatment level. In fact, in many cases it is possible to achieve treatment levels with this technology to allow direct discharge to waterways. Pilot testing demonstrated the feasibility of this process and established the parameters for a commercial system. Although this technology proved effective in achieving the treatment standard, the capital cost of such a system was high.

Other technologies evaluated included ultra-violet light oxidation and chemical oxidation using hydrogen peroxide and Fenton's reagent (a ferrous iron salt). The combination of UV light and ozone oxidation has proved to be a potent treatment technique for many organic chemicals. The merging of these two strategies has demonstrated nearly 100% effectiveness in many applications. Unfortunately pilot testing on plant wastewater was unsuccessful because of frequent clouding of the UV lamp.

Chemical oxidation using hydrogen peroxide was tested in both bench and pilot plant scale. This process oxidizes the chemicals in the wastewater to less hazardous products. Original testing with this scheme did not demonstrate effectiveness in removing phenol down to the initial treatment standard of 19 ug/L. The remand of phenol prompted a reevaluation of this process as a possible treatment alternative. The difficulty with this technology, however, is the lack of selectivity for the oxidizing agents. Constituents which do not have to be removed will be oxidized at various rates which leads to excessive consumption of the oxidizing agent.

In the case of plant wastewater, the high levels of acetone caused the consumption level of hydrogen peroxide to be excessive. This also leads to excessive sludge generation which must be disposed of at an additional cost.

AIR STRIPPING

As mentioned above air stripping was tested and originally rejected because of its inability to remove phenol. When the regulations for phenol were remanded, the air stripping process was reexamined to reduce capital and operating cost. The simplicity of the system (see Figure 2) including minimal area for installation of equipment was also a factor in its selection.

The process of stripping or desorption involves the transfer of a volatile component from a liquid stream to an inert gas. This is the reverse of the more common chemical engineering operation of absorption which involves the transfer of a condensable compound to a liquid stream. In wastewater applications concentrations are fairly dilute and the equilibrium conditions are represented by Henry's law:

$$P = H*X \qquad (1)$$

where:

P = partial pressure of material existing over a solution of concentration X

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*PACT is a registered mark of Zimpro/Passavant, Inc.

Table 1 Henry's Law Constants at 25°C [4]	
Compound	Reported Value kPa m³/mole
Acetone	0.004
Benzene	0.55
Ethylbenzene	0.80
Toluene	0.67
Cumene	0.86

H = Henry's Law constant
X = Concentration

The constant H is really not a true constant and depends on the temperature. The magnitude of H is a measure of the relative ease of transfer of the contaminants to the air stream and therefore stripping rates are improved with temperature. Values for Henry's law constant, taken from the literature, for selected compounds in the plant effluent are shown in Table 1.

The height of packing [l] is determined using the transfer unit approach represented by the expression:

$$Z = HTU * NTU \qquad (2)$$

where:

Z = tower height

HTU = height of a transfer unit
$= V/K_L a \qquad (3)$
$K_L a$ = mass transfer coefficient per interfacial area for transfer

NTU = number of transfer units
$= (R/R - 1)\ln(((X_{in}/X_{out})(R - 1) + 1)/R) \qquad (4)$
$R = H * G/L \qquad (5)$

G = molar flow of gas
L = molar flow of liquid
X_{in} = influent concentration of compound
X_{out} = effluent concentration of compound

Inspection of the above relationships reveals that the first term, HTU, is a measure of the efficiency of the transfer and is influenced by parameters such as packing type and liquid distribution. Although models exist for a priori calculation of the mass transfer coefficient, these generally prove only accurate enough for preliminary design. Final designs are verified using pilot plant data for the system as was done for the proposed plant facility.

The second term in the expression incorporates the equilibrium considerations into the design. Note: that as the gas to liquid ratio increases, the stripping factor, R, increases re-

Table 2 Typical Pilot Plant Data [5]						
Liquid Flow—m³/hr			2.7			
Air Flow—m³/hr			425			
Air/Liq. Ratio			157			
Influent/Effluent Temp. °C			47/34			
Stripper Delta P—Pa			12.4			
Component Analysis:						
			Sample Location*			
	1	2	3	4	5	6
Acetone—mg/L	1623	1543	1263	844	436	376
Benzene—ug/L	304	27	<10	<10	<10	<10
Toluene—ug/L	93	30	TR.	TR.	TR.	TR.
Ethylbenzene—ug/L	<10	<10	<10	<10	<10	<10
Cumene—mg/L	157	42	14	5	1.3	1.4
AMS—ug/L	678	253	154	50	46	46

*Sample 1 and 6 are located in the influent and effluent streams respectively. The remaining four samples are located intermediate in the packing from top to bottom.
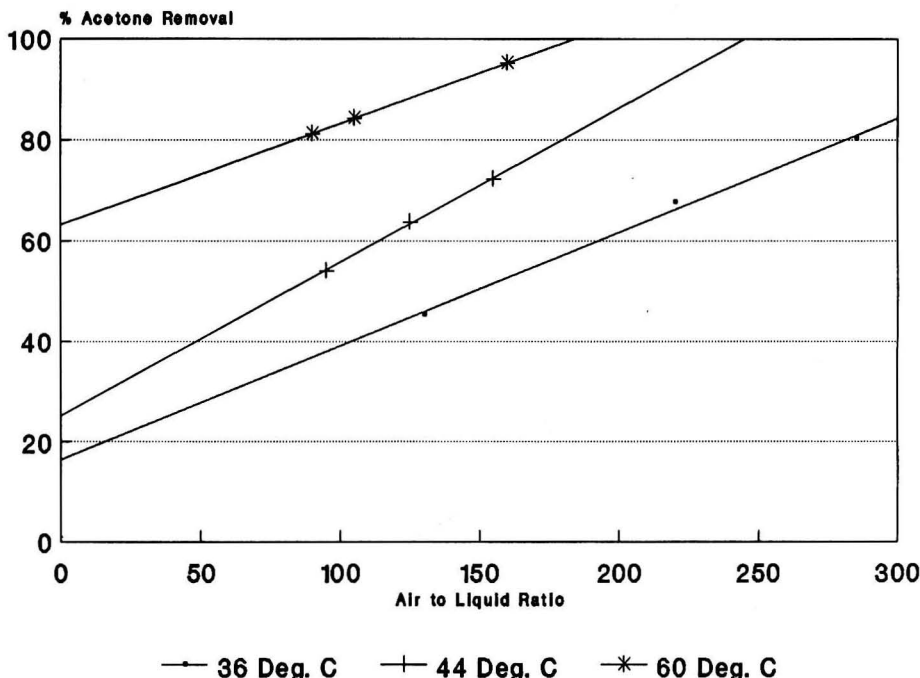

FIGURE 3. Acetone removal vs. temperature and A/L.

sulting in an improved separation. As mentioned previously the separation is easier the higher the Henry's law constant which increases with temperature.

The pilot unit used to predict performance for the commercial system consisted of a 16 inch (40 cm) diameter column with two 10 foot (3 m) sections of packing. Initial testing was done using 1 inch (2.54 cm) Jaeger Tri-Pac™ while additional testing was done using 1 inch (2.54 cm) Rauschert™ rings. Testing was done at various gas to liquid ratios and several liquid temperatures.

A typical set of data from the pilot testing is shown in Table 2. The concentration of several constituents are normally at such low levels that these compounds were introduced in the feed to verify design performance. These data show the relative ease in removing benzene while the removal of acetone is more arduous as evidenced by the relative difference in Henry's law coefficient. (In fact acetone is often removed from air streams by absorption into water.) The effect of air to water ratio and liquid temperature on the removal of acetone from the pilot plant is shown in Figure 3.

Although acetone is not a regulated compound, it was decided to optimize the removal of acetone to reduce overall plant discharges and to reduce the operating cost of the thermal oxidizer used to dispose of the gas stream from the stripper.

Based on the pilot plant performance, an air to water ratio of 100 to 1 was chosen for the full scale system. Although the 20 feet (6 m) of packing used in the pilot plant runs appeared adequate to remove the regulated compounds, an additional 10 feet (3 m) of packing was added to the commercial system to ensure performance and to provide additional removal of acetone. The diameter of the column was determined from hydraulic considerations using estimated packing factors. The design percent of flooding was chosen at 50% to minimize foaming tendency and to provide future expansion capability.

THERMAL OXIDIZER

A thermal oxidation system was selected to treat the contaminated air stream from the air stripper. It was chosen because of its high destruction efficiency and because it provides conclusive destruction without need for further processing. Thermal oxidation is a widely used technique and can be applied to liquids and vapors. The final products are mostly inerts.

The principle of thermal oxidation is based on the simple concept of combustion.

$$C_xH_{2y} + (x + y/2)O_2 \longrightarrow xCO_2 + yH_2O$$
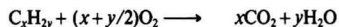
The oxygen required to ensure completion of this reaction is generally supplied by addition of ambient air. However, in this particular application, the vapor stream contained sufficient oxygen to complete the oxidation of the organic constituents and also the natural gas added for raising the temperature to the desired condition.

The vapor flow rate to the thermal oxidizer was designed based on the amount required for stripping while keeping the LEL (lower explosion limit) below the required level in the inlet gas to the thermal oxidizer. This was based on expected concentrations of organic constituents in the water stream. The organic concentration approximately followed a normal shaped distribution.

Normal design LEL is 25% but excursions are allowed if sufficient instrumentation such as LEL meters is provided. NFPA (National Fire Protection Association) guidelines require shutdown at 50% LEL level.

The major compounds in the air stream were identified as acetone and cumene. Their LEL's [6] at ambient conditions are as follows:

Acetone − 2.6%
Cumene − 0.88%

The LEL of a mixture [2] is calculated as follows:

$$LEL \,(Ave) = 100/(EC(i)/(LEL(i))) \qquad (6)$$

LEL (Ave) − Average LEL of mixture
EC(i) − Expected concentration of component i
LEL(i) − LEL of component i

The LEL of hydrocarbons [3] is also dependent on the temperature. The relationship is given by:

$$LEL(T) = LEL(25) * (1 - (0.75/LEL(25) * HC) * (T - 25)) \qquad (7)$$

LEL(T) − LEL at temperature T°C
LEL(25)   LEL at 25°C
T   − Temperature of gas °C
HC   − Net heat of combustion, kcal/mole

After review of safety requirements, the LEL of organic components was allowed to go as high as 40% as long as an LEL indicator was present in the air stream. This alteration allowed lowering the flow rate of air to approximately 60% of the earlier design resulting in lower capital costs for all equipment. Also, it reduced the operating costs in terms of electricity and natural gas requirements.

ENVIRONMENTAL REGULATIONS

The plant emissions are regulated by the City of Philadelphia. There is a limit on the emission of total hydrocarbons from the entire facility. Based on this requirement, the total hydrocarbons had to be reduced by a factor of 99%.

Future regulations may require a 99% destruction efficiency for individual components depending upon the final rules implemented under Clean Air Act. Since the final requirements under this act are not certain, it was decided to defer extensive design modifications to a later date. There are a number of options for design adjustments to meet these requirements in the future.

Since there were no published data available that would correlate destruction efficiency versus temperature and residence time for the specific components being handled, the design parameters were specified based on empirical data provided by several vendors. The data provided for a similar installation proved a destruction efficiency of 99% for acetone. Based on this information, it was decided to operate the system at a temperature of 1500°F (815°C) with a minimum residence time of 1.0 seconds.

TYPES OF THERMAL OXIDIZERS

Thermal oxidizers are refractory lined chambers with burners mounted for ignition of organic components and for the auxiliary fuel. The gases are heated to the oxidation temperature by combustion of organic components and natural gas.

There are two major options for thermal oxidizers—thermal and catalytic. Both these systems have their advantages and disadvantages.

The catalytic thermal oxidizers (Figure 4) involve heating the gases up to a temperature of approximately 550-700°F (288-371°C). The gases then pass through a catalytic bed where the oxidation of organic components is completed. This unit could probably provide the destruction efficiency required for the total hydrocarbons although the amount of catalyst required would be difficult to estimate without testing. The ben-
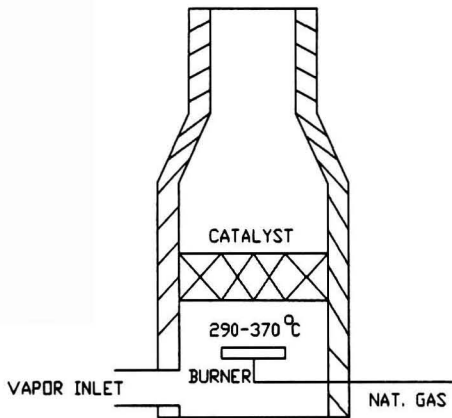
FIGURE 4. Catalytic thermal oxidizer.

efit from using this type of system is lower fuel costs. This is because the catalytic systems operate at a lower temperature of 550–700°F (288–371°C) as compared to thermal oxidizers which require that gases to be heated as high as 1400–1500°F (760–815°C).

In this application, the fume already contained a significant amount of organic constituents. Therefore, the fuel savings would have been minimal. A detailed analysis indicated several other concerns.

1) If the organic constituents concentration surged above a certain value, outside air would have to be introduced to keep the catalyst cool.

2) High temperature could also destroy the effectiveness of the catalysts.

3) The fouling of the catalysts from contaminants in the air stream would have required frequent changing of the catalyst resulting in higher operating costs.

The thermal oxidizer was determined to be a more suitable alternative for this application. Preliminary contacts with leading thermal oxidizer vendors established their confidence in meeting performance requirements with proven designs. Also,

an analysis of thermal oxidizers indicated that capital and operating expenses were competitive as compared to catalytic systems. A site visit was undertaken to confirm the operating experience of this type of system. Also, a number of other facilities were contacted to get an insight into the concerns of other users of this type of system.

HEAT RECOVERY

The organic constituents in the air stream stripped from the waste water had a heating value of 3.3 MM Btu/hr (3481 MJ/hr) associated with them. However, it was not enough to reach the oxidation temperature of 1500°F (815°C). Therefore, 170 SCFM (4.8 Nm³/min) of natural gas was required to bring it up to the design oxidation temperature. With a straight through system, this heat input would have been 10.7 MM Btu/hr (11,290 MJ/hr). This would incur an annual operating cost of $750,000. Since this would have been a substantial operating cost, heat recovery was evaluated for reducing fuel costs. The addition of a heat exchanger also prevents flashback, provided the velocities were kept above the flame front velocities.

The two alternatives for heat recovery were recuperative versus regenerative.

The recuperative systems (Figure 5) involve heat recovery using plate type or shell and tube type heat exchanger. These systems generally recover 60–70% of the heat input. They are cheaper in costs, but they have a problem with leakage because of metal expansion at high temperatures. The shell and tube type systems require frequent maintenance for repairing welds. The plate type systems have an inherent leakage possibility because of the design. This leakage can be as high as 0.5% of total air flow. Choosing this type of heat exchanger requires a minimum destruction efficiency of 99.5% in the combustion chamber in order to have an overall efficiency of 99%.

The regenerative systems (Figure 6) involve alternate heating and cooling of stoneware beds. The heat recovery for these type of systems is generally in the range of 90–95%. They are lined with high temperature refractory, therefore they are more forgiving with respect to temperature excursions. The stoneware beds also acts as a flame arrestor. The drawbacks for these systems include the necessity for control valves which
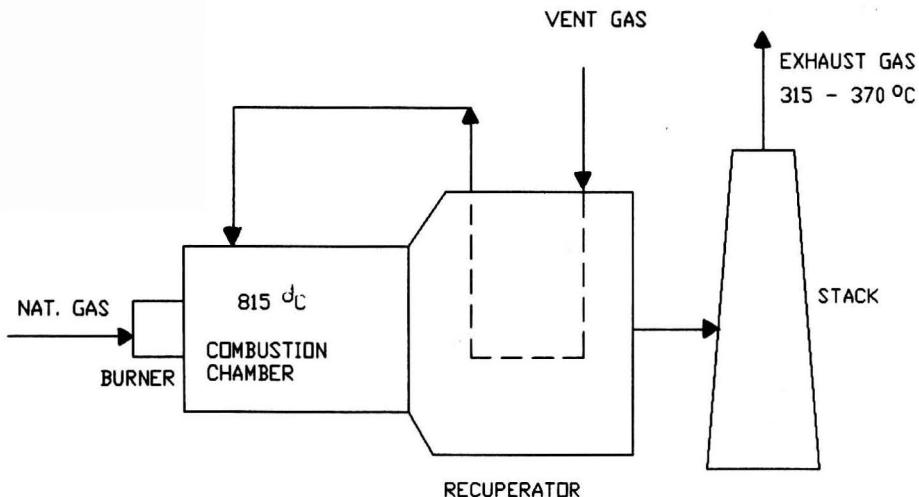

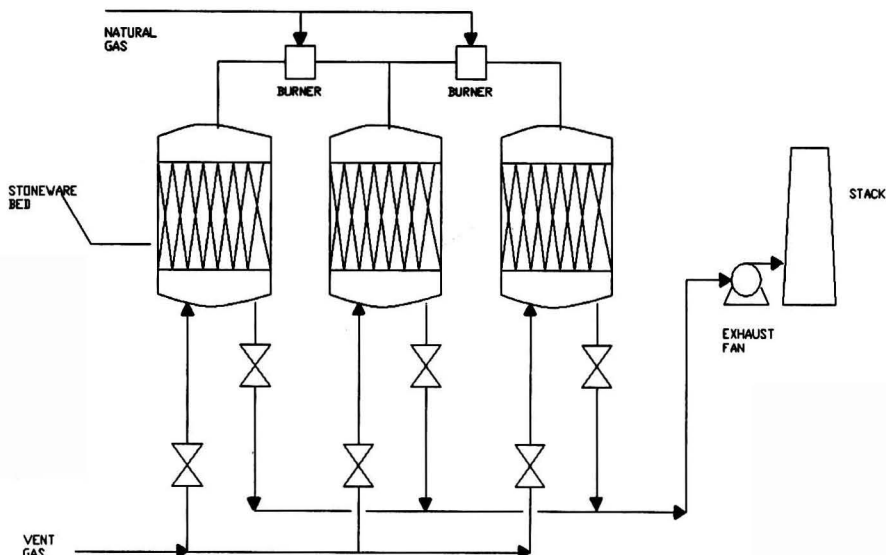FIGURE 5. Thermal oxidizer with heat recuperator.

FIGURE 6. Thermal oxidizer with regenerative type heat exchanger.

are constantly closing and opening. They also involve very high capital costs.

Since the air stream for this application already included a substantial amount of organic constituents, the savings in fuel costs was not sufficient to justify the extra capital costs for the regenerative bed system. In fact the heat input was too great for this application under high concentration of organic constituents. In this instance the system would have required introduction of additional ambient air to prevent excursion of temperature. Because of these problems, the option of regenerative heat recovery was discarded. Instead, a recuperative type system was chosen with a plate and frame heat exchanger.

Flame safeguards and shutdown interlocks are provided for the systems in accordance with industry standards and internal company guidelines. Under the control strategy, the first step involved cutting back the natural gas flow to the combustion chamber to an absolute minimum. If the temperature in the combustion chamber continues to increase, part of the hot gases would bypass the heat exchanger and exhaust to the stack. If the hot gas bypass valve is completely open and the temperature continues to increase, the unit would automatically shut down at a predetermined temperature level. The system would then be restarted at a reduced water flow to the stripper until the concentration of organics is reduced. Currently, there is no continuous monitoring required on the stack exhaust. The operating parameters will be verified by measuring emissions during test burn.

CONCLUSION

Various process technologies exist for treating wastewater in order to comply with various environmental regulations including the OCPSF standards. The choice of technology to use is contingent on the nature of the contaminants in the waste stream. In this particular application air stripping was shown to be a cost effective approach to fulfill the requirements. Its use with this particular wastewater stream was highly effective because the compounds to be removed were suffi-

ciently volatile. For less volatile constituents, including phenol if reregulated, one of the other treatment techniques discussed should be evaluated. Finally, the vapor stream containing the contaminants can be efficiently converted to carbon dioxide and water in a thermal oxidizer with heat recovery. Because of the heating value of the compounds in the vapor stream, a thermal oxidizer was determined to be more suitable than a catalytic or regenerative type unit for this application.

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Nucleation and Crystal Growth of Calcium Sulfite Hemihydrate

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In slurry scrubbing processes for flue gas desulfurization the precipitation rate of calcium sulfite affects scrubber solution composition, SO_2 absorption, sulfite oxidation, and limestone utilization. Sludge quality and disposal costs are also a function of precipitation kinetics. The nucleation and crystal growth rates of calcium sulfite hemihydrate were measured in a continuous flow crystallizer at conditions that produced agglomerate crystals. At 28 and 55°C, the nucleation rate, $B°$, varied from 0.25 to 23 $\times$ 10^8 #/m^3-sec and was given at pH 5.5 by the correlation:

$$B° = 2.7 \times 10^{18} exp\left(\frac{-4 \times 10^3}{RT}\right) M_T^{1.0} G^{1.0} \qquad (12)$$

The suspension density, M_T, was varied from 7 to 90 kg/m^3. The linear growth rate, G (m/sec), varied from 0.5 to 9 $\times$ 10^{-9} m/s as residence time was varied from 42 to 360 minutes. The nucleation rate constant had a maximum near pH 5.5 and was about 50% lower at pH 4.2 and pH 6.5. Gypsum saturation in solution caused both the nucleation and growth rates to decrease.

INTRODUCTION

Nucleation and crystal growth of $CaSO_3$/$CaSO_4$ are important in FGD systems because they effect the scrubber solution composition. Therefore, they can also affect SO_2 absorption, sulfite oxidation and lime or limestone dissolution [4, 10]. Since stack gases contain oxygen, some of the sulfate will be oxidized to sulfate. A mixture of $CaSO_3$/$CaSO_4$ is obtained as the product. The sulfate content of the solids can effect the crystal size and shape. Crystal size and shape determine the ease of dewatering and thus the economics of waste disposal.

A significant amount of work has been done to characterize and improve the quality of the flue gas scrubber sludge. Philips et al. [18] evaluated sludges from limestone and lime scrubbing systems. The limestone sludge contained platelet shaped calcium sulfite hemihydrate crystals. Solids from the lime sludge were rosette shaped. The settled density for the limestone sludge (48 wt. % solids) was greater than that for the lime (34 wt. % solids). This results in easier dewatering of the limestone sludge.

Ottmers et al. [16] performed experiments to measure the precipitation rate of calcium sulfite. The rate was found to be first order relative to the supersaturation of calcium sulfite. Meserole et al. [15] determined the effects of high concentrations of dissolved ions on the precipitation of calcium sulfite hemihydrate, gypsum and a solid solution of calcium sulfite/calcium sulfate.

Jones et al. [11] confirmed the formation of a solid solution of calcium sulfite/calcium sulfate hemihydrate using x-ray diffraction and infrared spectroscopy. Setoyama and Takahashi [25] determined that sulfate substitutes for sulfite in calcium sulfite hemihydrate and that the substitution is a function of reaction temperature. The calcium sulfate content in calcium sulfite hemihydrate was 10 wt. % at 15°C and increased to 22 wt. % at 83°C.

Tseng and Rochelle [28, 29] determined the dissolution and crystallization rates of calcium sulfite in aqueous solutions as a function of pH, dissolved sulfite and sulfate, and temperature. The dissolution rate was accurately modeled by assuming

Table 1 Summary of Power Law Expressions: Previous Work

Compound	Power Law Expression	Reference
CaSO$_3$/CaSO$_4$ in Mg-Lime Systems	$B° = k_n G^{0.63} M_T^{2.6}$	Randolph et al., 1988
CaSO$_3$/CaSO$_4$ (with Cl$^-$)	$B° = k_n G^{1.1} M_T^{0.6}$	Alvarez-Dalama, 1986
(with SO$_4$=)	$B° = k_n G^{1.1} M_T^{2.2}$	
CaSO$_3$/CaSO$_4$	$B° = k_n G^{0.94} M_T^{1.1}$	Kelly, 1983
CaSO$_4$½H$_2$O	$B° = k_n(T) G^{3.19}$	Sikdar et al., 1980
CaSO$_4$2H$_2$O	$B° = k_n G^{1.48} M_T^{1.27}$	Etherton & Randolph, 1981
CaCO$_3$/Mg(OH)$_2$(no iron)	$B° = k_n G^{2.0}$	Peters & Stevens, 1982
(with iron)	$B° = k_n G^{13.9}$	
Borax	$B° = k_n G^{1.48} M_T^{0.84}$	Randolph & Puri, 1981
NH$_4$NO$_3$	$B° = k_n G^{1.22} M_T^{0.98}$	Youngquist & Randolph, 1972
NaCl (marine propeller)	$B° = k_n(RPM)^2 G^2 M_T^1$	Grootscholten et al., 1982
(pitched blade)	$B° = k_n(RPM)^{2/3} G^2 M_T^1$	
KCl	$B° = k_n(RPM)^k G^{1.67-2.95} M_T^{0.7-1.21}$	Quin et al., 1987

the solids are spherical particles in an infinite stagnant solution and accounting for the effect of solution equilibria on the mass transfer driving force. The crystallization rate (correlated with BET surface area rather than size) was found to be second order relative to the calcium sulfite supersaturation. The presence of sulfate in solution reduces both the dissolution and crystallization rates. Several different seed crystals were used in these studies. They varied in sulfate content and crystal habit (agglomerates and rosettes). Gleason and Rochelle [8] arrived at similar conclusions with calcium sulfite platelets.

Kelly [12] measured the growth rate of calcium sulfite. He also performed experiments to determine the effects of various chemical additives on the metastable limit and the crystal habit. Alvarez-Dalama [1] performed experiments to determine the nucleation and crystal growth rates of calcium sulfite. Also investigated were the effects of high chloride, magnesium, and sodium levels on the crystal habit. Both Alvarez-Dalama and Kelly used a mixed-suspension-mixed-product removal (MSMPR) crystallizer and analyzed the data by the population balance approach. This has the advantage that both nucleation and growth rate determinations can be made at the same time.

Benson et al. [2] studied calcium sulfite crystallization in the magnesium-lime system. Their laboratory experiments confirmed industrial experience in which longer residence times and higher solids density resulted in smaller particles. This is the opposite of what occurs in limestone systems. The crystals that form in magnesium-lime systems are rosettes comprised of thin platelets. The rosettes are more susceptible to breakage by agitators and pumps than the thicker platelet crystals formed in limestone systems.

A variety of related crystallization systems have been investigated by other researchers. Table 1 is a summary of the power law kinetic expressions that were determined for CaSO$_3$ and other compounds. The nucleation rate, $B°$, is given as a power function of the crystal growth rate, G, and the solids concentration, M_T. These results can be used to analyze CaSO$_3$/CaSO$_4$ crystallization. Secondary nucleation has been found to be the dominant nucleation mechanism in crystallizers with significant solids concentration. Therefore, CaSO$_3$/CaSO$_4$ data can be correlated using a power law kinetic expression. Propeller type, level control and adequate mixing are a few important considerations in crystallizer design. Deviations from ideal behavior (size independent growth) must be analyzed carefully since a number of factors can give the same results. Impurities and additives can have a dramatic effect on crystallization kinetics. This can be seen in the kinetic order on the growth rate for the CaCO$_3$/Mg(OH)$_2$ system [17]. When iron is present the kinetic order increases from 2.0 to 13.9. This indicates a drastic decrease in the crystal growth rate of CaCO$_3$. Iron poisoned the surface of the crystals and therefore reduced the amount of scale adhering to the reactor walls. Impurities are particularly important in FGD systems where

manganese, magnesium, aluminum, chloride, iron, adipic acid and thiosulfate are a few impurities and additives present.

In general, if the exponent on the growth rate is near 1.0, the particle size distribution does not increase if the solids residence time in the reactor is increased. This is because the product of growth rate and residence time is constant [21]. Also, if the exponent on the solids concentration is near one, the shape of the particle size distribution curve is independent of the solids concentration.

In this paper a mixed-suspension-mixed-product-removal (MSMPR) reactor was used to measure the nucleation and crystal growth rates of calcium sulfite hemihydrate. The effects of pH, solution sulfate concentration, solids residence time, solids concentration and temperature on nucleation and growth kinetics were investigated. The product crystals were characterized using scanning electron microscopy, iodine titration, BET surface area (for representative solids only) and Coulter Counter particle size analysis.

THEORY

Nucleation

There are three mechanisms of nucleation: 1. Homogeneous—formation of new crystals due to only the liquid supersaturation; 2. Heterogeneous—formation of new crystals due to the presence of foreign insoluble material; 3. Secondary—formation of new crystals in the presence of the same type of crystals.

In industrial crystallizers, secondary nucleation is the most important mechanism. Clontz and McCabe [5] demonstrated that contact energy and supersaturation are important factors in new crystal formation. An empirical power law expression has been found to adequately predict the nucleation rate ($B°$) for most secondary systems. Equation 1 is the power law equation which shows that the nucleation rate is a function of the suspension density (M_T) and supersaturation (s).

$$B° = k_n M_T^i s^j \tag{1}$$

Crystal Growth

Crystal growth can be characterized by a three-step mechanism: 1. Diffusion of solute to the crystal surface; 2. Adsorption of the solute onto the crystal surface; 3. Integration of solute into the crystal lattice. In a stagnant solution the linear crystal growth rate (G) is usually limited by the diffusion rate and therefore proportional to the supersaturation (s).

$$G = \frac{dL}{dt} = ks \quad (2)$$

For agitated solutions the surface integration step usually controls. Burton et al. [3] state that growth along screw dislocations is the most probable. This is represented by:

$$G = ks^2 \quad (3)$$

Other mechanisms have been proposed such as the spiral growth mechanism by Van Rosmalen [30] for low values of supersaturation. He also stated that for high supersaturations growth may be due to polynuclear surface nucleation. These mechanisms cannot be related to a second order function of supersaturation. To account for the variety of growth mechanisms a power-law type expression is used (Equation 4). Values of (a) range from one to two.

$$G = ks^a \quad (4)$$

The growth rate expression can be used to eliminate the supersaturation term in the power law expression (Equation 5).

$$B^\circ = k_n M_T^i G^j \quad (5)$$

Population Balance

The crystallization process can be described in terms of a population balance. It accounts for particles entering and leaving the system, and growth and breakage of existing particles. The population balance for a system as derived by Randolph and Larson [21] is shown in Equation (6).

$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial L} + D - B + \frac{nd(\ln V)}{dt} = -\sum_k \frac{n_k Q_k}{V} \quad (6)$$

For a steady-state system where breakage is negligible, and there are no particles in the inlet streams, Equation 6 reduces to:

$$\frac{\partial Gn}{\partial L} + \frac{nQ}{V} = 0 \quad (7)$$

When the growth rate is independent of crystal size (McCabe's ΔL Law, [14]) Equation (7) can be easily integrated to:

$$n = n^\circ \exp\left(-\frac{L}{G\tau}\right) \quad (8)$$

Substitution of the definition of the population density (Equation 9) into Equation (8) and integration from size L to infinity results in an expression for the cumulative size distribution (Equation 10).

$$n = \frac{dN}{dL} \quad (9)$$

$$N_L = n^\circ G\tau \exp\left(-\frac{L}{G\tau}\right) \quad (10)$$

A plot of $\ln N_L$ versus L should result in a straight line with an intercept of $\ln(n^\circ G\tau)$ and slope of $-\frac{1}{G\tau}$. The nucleation rate can be determined from Equation (11).

$$B^\circ = \left(\frac{dN(L)}{dt}\right)_{L \to 0} = \left(\frac{dN(L)}{dL}\right)_{L \to 0}\left(\frac{dL}{dt}\right) = n^\circ G \quad (11)$$

EXPERIMENTAL APPARATUS AND PROCEDURE

The pH-stat apparatus was modified from a semibatch system (Gleason and Rochelle, [8]) to a continuous mixed-suspension-mixed-product-removal (MSMPR) reactor in order to measure the nucleation and crystal growth rates of calcium sulfite hemihydrate (Figure 1). It consisted of a jacketed, 500 mL agitated reactor with nitrogen sparging. The lid was a rubber stopper (4 cm thick) that fitted tightly in the reactor. There were holes drilled into the stopper for the agitator, thermometer, feed streams (5 cm apart), pH electrode and titrant delivery tube. The agitator was a three blade marine-type propeller. The two feed streams ($CaCl_2$ and Na_2SO_3/Na_2SO_4 mix) were fed by a dual head MasterFlex peristaltic pump with a 10 turn potentiometer speed control. The motor speed range was 1 to 100 rpm. Size 13 tubing was used which corresponds to feed flow rates from 0.5 ml/min to 7 ml/min. All feed streams are fed below the liquid level. Fine tuning of the reactor pH was done with the pH stat apparatus using 1.0 M HCl as the titrant. Titrant delivery was also below the liquid level.

Level control was achieved with a MasterFlex peristaltic pump with size 16 tubing. The end of the tubing was cut at a slant and a small hole (0.5 cm in diameter) was cut 1 cm above the slant. The level control tubing was placed in the reactor with the small hole at the desired liquid level. This was done to ensure that the contents of the exit stream were the same as the contents of the reactor. The peristaltic pump was set to pump at 25 ml/min.

Prior to all experiments the agitator and peristaltic pumps were calibrated. All experiments were performed with an agitator speed of 370 rpm. Higher speed caused the liquid level to vortex around the agitator shaft. Lower speed did not produce adequate mixing.
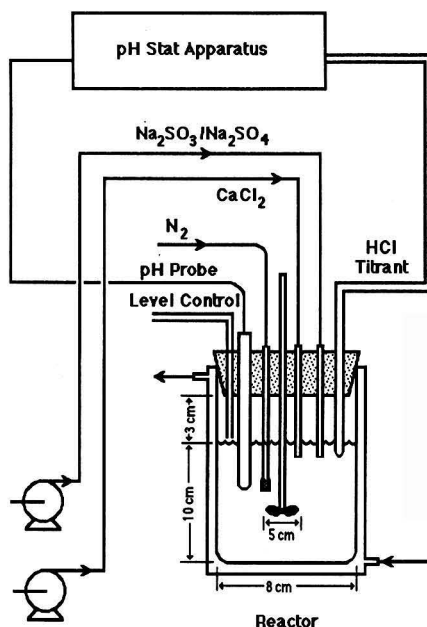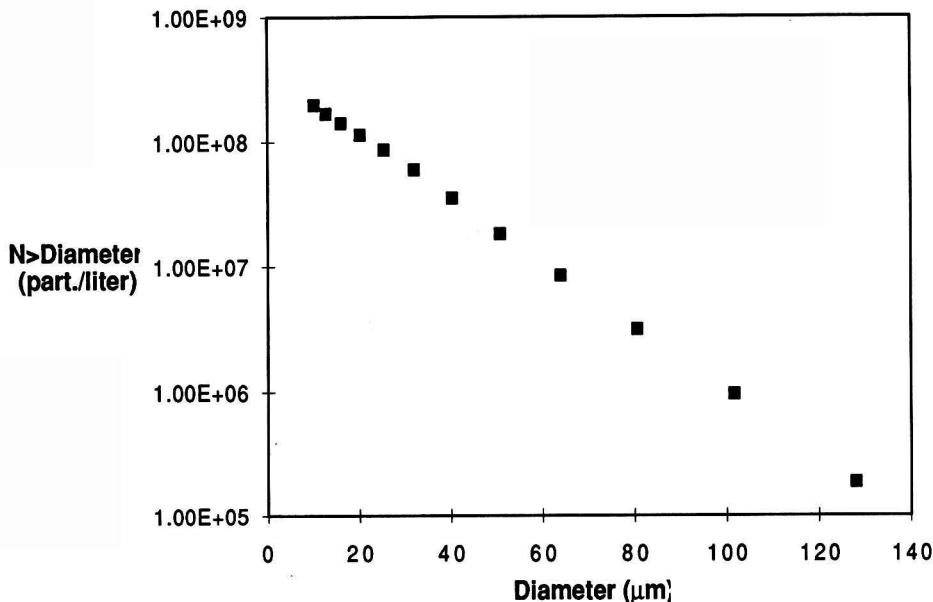

FIGURE 1. Experimental Apparatus

FIGURE 2. Typical Experimental Results Experiment G-30 (pH = 6.5, T = 55°C, τ = 42 min.)
Feeds: 0.3M $CaCl_2$, 0.08 M Na_2SO_3/0.02 M Na_2SO_4

Initially, the reactor was filled with 500 ml of 0.1 M $CaCl_2$ solution. This was sparged with oxygen free nitrogen for approximately one-half hour while heating up to the desired temperature (55°C). The pH electrode was calibrated at the reactor temperature with a pH 7 buffer (potassium phosphate monobasic (0.05M)—sodium hydroxide and a pH 5 buffer (adipic acid (0.005M)—sodium hydroxide, in 0.1M calcium chloride). Then 3–5 ml of 0.5M Na_2SO_3 was added to the reactor and the pH was adjusted to the desired value. The feed and level control pumps were started and the pH stat apparatus turned on.

During each experiment the reactor pH and titrant demand were recorded on a strip chart recorder. The flow rate of the exit stream was also monitored using a graduated cylinder and stop watch method several times during the experiment. The experiment was allowed to run for 6–7 residence times before slurry samples were taken for analysis.

Approximately 40 ml of slurry was removed from the reactor with the level control tubing immersed in the reactor. Ten ml of this slurry was filtered with a 0.5 micron Millex filter unit. The clear solution was immediately placed in a small sample vial and capped. It was later (within 15 minutes) analyzed for total sulfite content using iodine titration. One ml of the slurry sample was placed in 200 ml of 4 weight percent $CaCl_2$ (filtered to 0.5 microns) for analysis in a Coulter Counter TAII using a 400 micron aperture. The number of particles per ml and the particle size distribution of the slurry were measured. Slurry samples were taken 2–4 times before the experiment ended at approximately 11 residence times. The contents of the reactor were vacuum filtered, rinsed with approximately 100 ml of distilled water, vacuum dried of 80°C, weighed and saved for later analysis.

It was found that after approximately seven residence times the number of particles per ml (N_T) varied ± 10 percent. The particle size distribution was also constant after seven residence times (each channel was ±10 percent of its previous value). This was the experimental error of the Coulter Counter measurement. The experiment was considered to be at steady state

when 2–3 successive samples were analyzed and did not vary more than 10 percent.

The data from the Coulter Counter was used to calculate the nucleation and crystal growth rates. For example, a plot of Log N_L (cumulative number distribution) as a function of L (particle size) is shown in Figure 2 for Experiment G-30. From the intercept the nucleation rate is calculated to be 1.5 ± 0.2 × 10^8 #/m^3-sec. The slope results in a linear growth rate of 6.7 ± 0.1 × 10^{-9} m/sec. This typical experiment produced solids that were rosette shaped. They varied in size from 10 to 160 μm. The average particle size was approximately 40 μm. The calcium sulfite hemihydrate content was 85 ± 3 weight percent and the BET surface area was 4.2 ± 0.1 m^2/gram.

The effects of slurry solids concentration, solids residence time, pH, gypsum saturation, and temperature on the nucleation and growth rates were investigated. The product solids were characterized using scanning electron microscopy to determine crystal habit, iodine titration to determine sulfite content, and N_2 absorption to determine BET surface area (for representative solids only).

RESULTS AND DISCUSSION

The nucleation and crystal growth rates of calcium sulfite hemihydrate were measured in a continuous flow crystallizer. The residence time of the solids was varied from 40 to 360 minutes. The solids density was varied from 7 to 90 g/liter. The reactor pH was varied from 4.25 to 6.5. The majority of the experiments were performed at 55°C, but a few were performed at 25°C to determine the effect of temperature on the nucleation and growth rates. The gypsum saturation in the reactor was approximately 1.0 with a Ca^{++} concentration of 100 mM for these experiments.

To determine the effect of gypsum saturation on the nucleation and growth rates, the gypsum saturation in the reactor was varied from zero to 0.7 with a Ca^{++} concentration of 1 mM. The pH was 6.5 to 6.75.

Table 2 Summary of Experimental Data

Exp. #	S(IV) (end) (mM)	M_T (end) kg/m³ Meas.	Pred.ᵃ	$B° \times 10^{-8}$ (#/m³-sec) Meas.	Pred.ᵇ	$G \times 10^9$ (m/sec)	pH	τ (min)
Base Case								
(55°C, Feed Streams: 0.3M CaCl₂, 0.08M Na₂SO₃/0.02M Na₂SO₄)								
G-13	3.5	5.7	6.0	2.0	1.9	5.2	5.5	42
G-20	2.7	6.8	6.0	2.3	1.9	5.3	5.5	42
Effect of Suspension Density								
(2,4,4,12 times base feed concentrations for Na₂SO₃/Na₂SO₄ and CaCl₂)								
G-22	3.2	15.0	13.2	3.3	4.2	5.5	5.5	42
G-31	2.4	26.5	27.0	3.5	3.7	1.6	5.5	125
G-21	2.7	44.3	27.0	17	7.9	5.0	5.5	42
G-19	4.2	81.5	79.8	23	23	5.0	5.5	42
Effect of Residence Time								
G-24	2.1	6.3	6.1	1.1	0.68	1.9	5.5	125
G-25	2.3	6.7	6.1	0.25	0.16	0.46	5.5	360
Effect of Temperature (28°C)								
G-26	3.8	4.5	5.7	1.4	1.8	5.2	5.5	42
Three Feed System								
(55°C, 0.36M CaCl₂, 0.096M NaHSO₃/0.024M Na₂SO₄, 0.275M NaOH)								
G-15	1.7	8.9	6.3	1.5		9.0	6.0	42
G-16	0.8	7.8	6.2	1.1		9.0	6.5	42
Effect of Gypsum Saturation								
(55°C, 0.3M CaCl₂, 0.1M Na₂SO₃/0 M Na₂SO₄)								
G-23	1.6	6.0	6.3	1.0		6.8	6.5	42
(55°C, 0.1M CaCl₂, 0.3M Na₂SO₃/0 M Na₂SO₄)								
G-33	100	5.8	6.3	6.2		4.9	6.75	42
(55°C, 0.1M CaCl₂, 0.12M Na₂SO₃/0.16M Na₂SO₄)								
G-36	12	6.9	6.3	1.4		9.0	6.75	42
Effect of pH								
G-35ᶜ	26.0	8.0	8.7	1.7		7.4	4.25	42
G-27	19.3	2.6	3.3	0.52		7.5	4.5	42
G-30	0.9	6.0	6.3	1.5		6.7	6.5	42
G-28	1.3	8.0	6.2	1.4		7.0	6.5	42

ᵃCalculated from material balance
ᵇCalculated from Eq. 12 with $k_n = 2.7 \times 10^{18}$ #/kg-m
ᶜFeed concentrations double base case for Na₂SO₃/Na₂SO₄ and CaCl₂

A summary of the experimental data is contained in Tables 2 and 3. Most of the results are represented well by a power law equation (Equation (12)) that gives the nucleation rate, $B°$ (#/m³-sec) as a function of the suspension density, M_T (kg/M³) and the linear growth rate, G (m/sec).

$$B° = k_n \exp\left(\frac{-4 \times 10^3}{RT}\right) M_T^{1.0} G^{1.0} \qquad (12)$$

$k_n = 2.7 \times 10^{18}$ # kg-m at pH = 5.5

and gypsum saturation = 1.0

Effect of Residence Time

The nucleation and crystal growth rates were determined at three different residence times: 40, 125, and 360 minutes. The suspension density was constant. The power law expression (Equation (11)) can be used to determine the kinetic order j which relates the nucleation rate to the crystal growth rate. It was observed that the particle size distribution is independent of the residence time.

Figure 3 is a plot of log $B°$ (nucleation rate) as a function of log G (growth rate). The slope of this line is $j = 0.9 \pm 0.1$. Alvarez [1] reported a value for the growth rate order of 1.1. Kelly [12] also reported values of 0.94 and 1.1. His results also indicated that j does not vary significantly as a result of impurity addition to the solution. These results were obtained using significantly smaller residence times (10 to 30 minutes), smaller suspension densities (1 kg/m³), and a significantly different experimental apparatus. The fact that $j = 1$ implies that the growth rate and the nucleation rate have the same dependence on solution saturation.

Benson et al. [2] used a power law model with a factor included to account for the power transferred to the slurry by the agitator. The experimental apparatus was much different than the one used in this study and others. It consisted of an 11.4 liter crystallizer with draft tubes and baffles. SO₂ was

Table 3 Effect of Gypsum Saturation

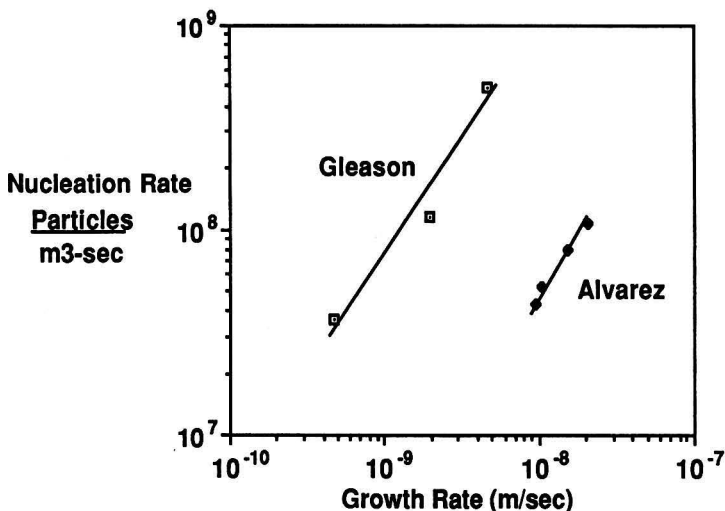| Exp.	S(IV) Ca⁺⁺ M/M	S(VI) Ca⁺⁺ M/M	$k_n \times 10^{-19}$ (#/kg-m)	RS Gypsum	Ca⁺⁺ mM	S(IV) mM	CaSO₃·½H₂O wt %
G-33	3.0	0	12	0	0.6	100	98
G-36	1.2	1.6	1.0	0.22	0.8	12	86
G-28	0.27	0.07	1.2	1.0	100	1.3	81

FIGURE 3. Plot to Determine the Growth Rate Order. Effect of Residence Time

directly bubbled into the reactor or sulfurous acid was one feed stream. The second feed stream was a lime/magnesium hydroxide mixture. There was also a high speed centrifugal pump that circulated the calcium sulfite solids between the crystallizer and an external vessel. They reported a value for the growth rate order of 0.63. The shear stresses imposed on the particles by the circulating pump caused the average particle size to decrease when the residence time increased. In general, previous researchers have presented little theory to explain observed growth rate orders. In the absence of known inhibitors, observed growth rate orders are in the range of 0.6 to 2.0.

Since the presence of additives, residence time, suspension density and reactor configuration (with low shear stress imposed on particles) do not affect the value of j significantly, j is set equal to 1.0. A kinetic order of 1.0 means that the growth rates change in proportion with the ratio of the residence times (Equation 13). Also, the particle size distributions of the solids for different residence times are the same. This is because the slope of the line in the cumulative population plot (see Figure 2) is obtained by the particle size distribution. The slope is $1/G\tau$ and since $G\tau$ is constant, the particle size distributions are the same. Therefore, larger particles cannot be obtained at longer residence times.

$$G_1\tau_1 = G_2\tau_2 \qquad (13)$$

However, the size of calcium sulfite particles have been found by other investigators to be sensitive to the shear stress imposed on them by agitation and circulation pumps. This causes smaller particles to be generated at longer holding times. Different crystallizer configurations may have different growth rate orders.

Effect of Suspension Density

The nucleation and crystal growth rates were determined at four suspension densities from 7 kg/m³ to 90 kg/m³. The residence time was held constant at 42 minutes. The power law expression (Equation 11) was used to determine the kinetic order i, which relates the secondary nucleation rate to the solids in suspension (M_T^i).

Figure 4 is a plot of log $B°$ (nucleation rate) as a function of log M_T (suspension density). The slope of this line is 1.0 ± 0.2. Therefore, the nucleation rate is proportional to the suspension density. Table 2 contains the experimental data for the different suspension densities and shows that the growth rate is the same to within 10 percent except for Experiment G-31. Experiment G-31 was performed at a higher residence time (τ = 125 min.). Since the growth rate order is equal to 1.0, the product of the residence time and growth rate should be a constant (Equation 13). $G\tau$ for the short residence time experiments (42 min.) was 2.0×10^{-7}. Experiment G-31 had a $G\tau$ equal to 2.1×10^{-7}. Therefore, changing the suspension density of a system with linear secondary nucleation kinetics does not result in a size distribution change and the nucleation rate increases proportionally with the suspension density.

Other researchers studying calcium sulfite nucleation found that the reaction order i is sensitive to other ions present in solution and the configuration of the experimental apparatus. Kelly (1983) found that $i = 1.1$. Alvarez-Dalama [1] determined that i varied between 0.6 and 2.2 depending on whether Cl^- or $SO_4^=$ was present. Benson [2] with different feed streams, the presence of magnesium, and much larger scale experimental apparatus (with a circulating pump) determined that $i = 2.6$. This higher order means that smaller particles were obtained at higher suspension densities probably due to the high shear stress imposed on the particles.

Because i is greater than zero, this is a process of secondary nucleation. Nuclei are created by the interaction of solids with shear caused by pumps and agitation. This mechanism should give $i = 1$. It does not appear that nuclei are produced by solid/solid interactions. If solid/solid interactions were important, i would be greater than 1.

The suspension density was measured by collecting and weighing the solids at the end of each experiment. It was also calculated using the difference between the sulfite concentrations in the feed stream and the reactor. Table 2 also contains these results. In most experiments the measured M_T is approximately 10 percent higher than the predicted. Scale formation on the reactor sides would cause the measured values of M_T to be higher than the predicted values. Two experiments produced less solids than predicted. These experiments were performed at low temperature and low pH. The total sulfite in solution for these experiments was greater than the base
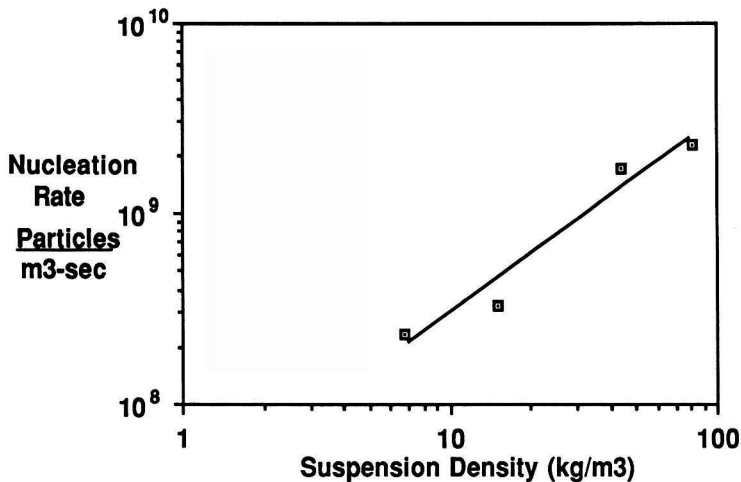
FIGURE 4. Effect of Suspension Density on the Nucleation Rate

case. This is expected since at low pH and low temperature the sulfite-bisulfite equilibrium favors bisulfite. There is more bisulfite in solution and therefore less calcium sulfite precipitated.

Experiment G-21 had a much higher suspension density (44 kg/m³) than the predicted value (27 kg/m³). In this experiment the $CaCl_2$ feed line split towards the end of the experiment. The Na_2SO_3 feed stream was still operating. Since the Ca^{++} ion is in excess, more solids precipitated than expected.

Effect of Temperature and pH

Experiments were performed at 28°C to determine the effect of temperature on the nucleation and growth rates. Table 2 shows that the growth rate is constant over this range, but the nucleation rate increases as the temperature increases. The activation energy for $CaSO_3\cdot\frac{1}{2}H_2O$ nucleation is estimated to be 4 ± 1 kcal/mol.

The significance of the activation energy is not apparent in this complex system. This is the activation energy for the nucleation rate as a function the growth rate. Tseng [27] found that the activation energy was 10 kcal/mol when he

related the growth rate as a function of calcium sulfite supersaturation to the second power. If we substitute his value of the activation energy into Equation 14 we get an activation energy of 14 kcal/mol when the nucleation rate is a function of calcium sulfite supersaturation. This is consistent with a surface kinetics mechanism, but changes in the rate expression will change the activation energy.

The nucleation and growth rates were determined for pH values of 4.25, 4.5, 5.5, and 6.5. The nucleation rate constant was calculated from Equation 12 for all pH values. Figure 5 shows the nucleation rate constant (k_n) as a function of pH. Although it appears that k_n has a maximum value near pH 5.5, an error analysis shows that the error in k_n is $\pm 35\%$ for any single value of k_n. This indicates that at low pH the value of k_n is significantly lower than at pH 5.5, but there is no significant difference in the nucleation rate constant between pH values of 5.5 and 6.5.

This may be an actual effect of pH or an effect of gypsum saturation (sulfate in solution). Since less solids precipitated at the low pH values, there was more sulfate in solution (higher gypsum saturation). Gypsum saturation decreases the nucleation rate constant.
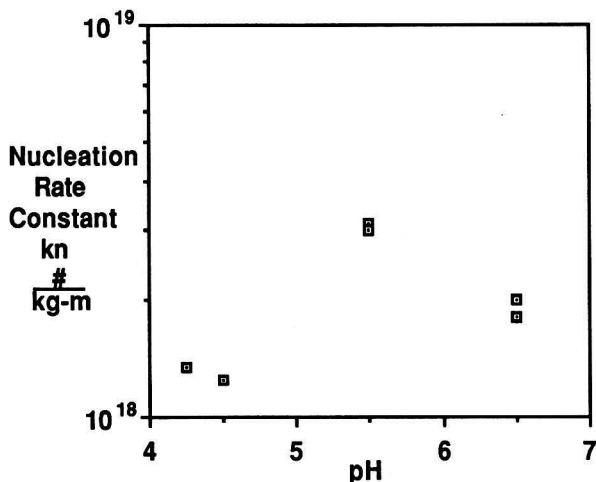

FIGURE 5. Effect of pH on the Nucleation Rate Constant, 55°C, 1.0 gypsum saturation.

Effect of Gypsum Saturation

The effect of dissolved sulfate (gypsum saturation) on the nucleation and growth rates was determined by a series of experiments in which the sulfate to calcium ion ratio $(S(VI)/Ca^{++})$ in the feed streams was varied from zero to 1.6. This corresponds to a change in gypsum saturation from zero to 1.0. Experiment G-28 had an excess of calcium ion while G-33 and G-36 were high in sulfite. The reactor pH was 6.5 to 6.75. Table 3 summarizes these results (see Table 2 for the complete experimental conditions). The nucleation rate constant (k_n) was calculated from Equation 12. Gypsum saturations were calculated using the Bechtel-Modified-Radian-Equilibrium Program (Lowell et al., [13]).

The weight percent $CaSO_3 \cdot \frac{1}{2}H_2O$ of the product solids was determined by iodimetric titration. Table 3 shows that when there is no sulfate added to the feed streams, the solids are 98 weight percent $CaSO_3 \cdot \frac{1}{2}H_2O$. As the gypsum saturation increases the weight percent $CaSO_3 \cdot \frac{1}{2}H_2O$ decreases. The $S(VI)$ to Ca^{++} ratio in the feed does not have a significant effect on the sulfite content of the solids. It is known that any sulfate in solution will end up in the solids up to approximately 80 weight percent $CaSO_3 \cdot \frac{1}{2}H_2O$ (Setoyama and Takahashi, [23]). Then if the gypsum saturation is greater than 1.0, gypsum will also be precipitated.

Comparison of Experiments G-36 and G-28 indicate that nucleation and growth kinetics are not a function of calcium concentration in solution. When there is no sulfate added to the solution the nucleation rate constant (k_n) increases by an order of magnitude over the experiments where sulfate is added. Clearly, the presence of sulfate in solution inhibits nucleation when expressed as a function of the growth rate. This was expected since in previous batch experiments (Gleason [8]), the presence of sulfate was found to inhibit both the dissolution and crystal growth rates of calcium sulfite hemihydrate. However, the nucleation rate is a stronger function of gypsum saturation than the growth rate when both are expressed as functions of calcium sulfite and gypsum supersaturation.

Since the nucleation rate is inhibited by the presence of sulfate (more so than the growth rate), larger particles should be formed in the presence of sulfate. Therefore, the use of oxidation inhibitors such as thiosulfate should actually reduce particle size because the gypsum saturation is very low. However, the dewatering properties of the low sulfate solids produced in the presence of thiosulfate are improved. Although the mean particle size is smaller or about the same, the particle shape is different. The low sulfate solids are thicker than the high sulfate solids (Gleason, [8]). These are the two seed crystals used in the batch experiments. They have about the same particle size distribution but were generated under potentially different nucleation conditions.

Growth Rate Correlation

The growth rate is typically predicted by a power-law type expression that relates the growth rate to the liquid supersaturation (Eq. 4). Unfortunately, iodimetric titration to determine the total sulfite in solution was not accurate enough to distinguish small changes in supersaturation. This occurs when the total sulfite is in the 1–10 mM range. For example, if the precipitation rate is 0.1 M in 42 minutes (as in experiment G-20) and it takes 30 seconds to take a sample, 1–2 mM of sulfite could easily be lost as the solution approaches saturation. BMREQ was used to calculate the supersaturations of the reactor solutions using the measured total sulfite. In all cases, the supersaturations were very close to zero. Other researchers also observed this [1, 12].

Three Feed System

The experimental apparatus shown in Figure 1 has two feed streams, $CaCl_2$ and a Na_2SO_3/Na_2SO_4 mixture. The feed streams were fed below the liquid level. The crystals formed in all of these experiments were rosette-shaped. There was some concern that there was inadequate mixing at the end of the feed tubes. This would result in areas of very high calcium sulfite saturation. The Bechtel-Modified-Radian-Equilibrium Program [13] was used to calculate the calcium sulfite relative saturations (RS_{CaSO3}) at the end of the feed tubes assuming an equal volume of feed and reactor solution for the base case experiment (G-20). At the end of the Na_2SO_3/Na_2SO_4 feed tube the RS_{CaSO3} is 15. The $CaCl_2$ feed tube end has a RS_{CaSO3} equal to 1.2. The bulk solution sulfite saturation is 1.0. In these areas there could be extremely fast nucleation resulting in rosette-shaped crystals.

Several experiments were performed with three feed streams to the reactor instead of two. The three feed streams were $CaCl_2$, NaOH, and $NaHSO_3/Na_2SO_4$ mix at flow rates that gave the same total reactor composition the same as the two feed system. The three feed system was investigated because at the ends of the three feed tubes there were not areas of high sulfite saturation. The RS_{CaSO3} at the end of the $NaHSO_3/Na_2SO_4$ feed tube was calculated to be 0.6. The $CaCl_2$ and NaOH feed tube ends had sulfite saturations of 2.5 and 0.5 respectively. Hopefully platelets would be formed. This was not the case. The crystals formed were rosette-shaped just as in the two feed system. In addition, pH control of the three feed system was difficult. The pH varied as much as 0.5 units above and below the desired pH. The nucleation rate constant (k_n) was calculated to be 1.1×10^{18} compared to 2.7×10^{18} for the two feed system. Considering the difficulty in pH control of the three feed system this was acceptable. Therefore, the two feed system was used for all other experiments.

There were no mixing problems detected in the batch crystallization experiments with the same reactor and agitation [7]. In these experiments 0.02 to 0.2 M Na_2SO_3 was titrated into 0.1M $CaCl_2$ using the pH stat apparatus. These concentrations are comparable to those in the two feed nucleation experiments. The crystal habit of the batch solids did not change from platelet to agglomerates. A crystal habit change would indicate nucleation in the mixing zone. Furthermore, the particle size distribution did not change in a direction that would suggest that nucleation is occurring as a result of poor mixing.

NOTATION

a = activity (mol/liter)
B = crystal birth function (#/m³-m-sec)
$B°$ = crystal nucleation rate (#/m³-sec)
D = crystal death function (#/m³-m-sec)
G = linear crystal growth rate (m/sec)
k = growth rate constant
k_n = nucleation rate constant
K_{SP} = calcium sulfite solubility product (mol/liter)²
L = crystal size (m)
M_T = total mass of particles (kg/m³)
n = population density distribution function (#/m³-m)
$n°$ = nuclei population density (#/m³-m)
N = cumulative number distribution (#/m³)
N_L = number of particles greater than size L (#/m³)
Q = volumetric flow rate (m³/sec)
RS = relative saturation of calcium sulfite hemihydrate ($a_{Ca^{++}} + a_{SO3} = ksp$)
s = supersaturation as 1-RS
t = time (sec)
V = total solution volume (m³)

Greek Symbols
τ = residence time (V/Q-sec)

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Computerized Batch Process for Treating Electroplating Wastes

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The application of batch processing to the treatment of electroplating wastes is described. The previously used continuous process proved to be unsatisfactory because of difficult and varying operating conditions over the treatment cycle and varying electroplating formulations. Consequently, a batch process was selected because of it is inherent advantageous in such cases. This study presents the reasoning behind this decision and describes the process and design factors that led to the particular facility.

INTRODUCTION

The Dan Region Association of Towns (DRAOT) sewage works collects and treats the municipal and industrial sewage of eight municipalities. The treated sewage is to be used for the irrigation of the Negev, an arid district in the south of Israel. The treated water processed by the plant must approach drinking quality. The DRAOT has established very strict standards for industrial discharge, and as a consequence, this often requires that effluents be pretreated at source.

Deutsch Ltd., was a subsidiary of Deutsch USA, a manufacturer of electromechanical aircraft devices in Rishon Lezion. Among its manufacturing stages is a metal treatment shop, which discharges its effluents via the Rishon Lezion municipality to the DRAOT treatment plant. In order to comply with the pretreatment standards, it was forced to install a pretreatment system.

In order to treat the wastes from their metal treatment shop, Deutsch Ltd., designed and constructed a continuous conventional treatment facility to destroy cyanides, to reduce the hexavalent chromine concentration and to eliminate all heavy metals by settling them as hydroxides. The operation of the continuous plant proved to be unsatisfactory, resulting in numerous conflicts with DRAOT inspectors. When the metal treatment facilities were enlarged, the necessity of a new and larger treatment plant became obvious. In the light of past experience, a thorough investigation was undertaken. As a result, Deutsch Ltd., decided to design and erect a batch treatment plant, based on an in-house design.[*] This paper presents the reasoning behind this decision, the inherent advantages in the design, and the rationale and design factors that led to the final plant implemented.

ADVANTAGES OF BATCH OPERATION

An effluent treatment plant constitutes a real chemical process. Although its product, treated water, does not bring monetary profits to its owner, substandard wastewater is usually penalized. In Israel, the scarcity of water gives an additional incentive to the utilization of treated effluent. In any case, effluent treatment is a necessary evil, whose costs should be

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[*]Since completing the first draft of this paper, Deutsch (Israel) Ltd., has undergone reorganizational changes, which also included the closure of the Rishon Lezion plant. The pretreatment plant was sold to Adar Gilshat Co. of Ashdod, who modified the unit to serve their plating activities.

Table 1 Maximum permitted concentrations of metal ions

Metal ion	Max. Concentration permitted per site[4] (mg/l)	Max. Concentration at DRAOT treatment plant inlet[5] (mg/l)	Load Capacity of DRAOT treatment plant (kg/day)
Zn	5.0	1.0	280
As	0.25	1.0	280
Al	25.0	2.5	700
Ag	0.05	0.25	70
Hg	0.005	0.25	70
Cr^{3+}	} 0.25	0.25	70
Cr^{6+}		2.5	700
Cu	1.0	1.0	280
Ni	1.0	0.25	70
Pl	0.25	1.0	280
Cd	0.05	2.5	700
Cn	2.0	20.0	5600

Table 2 Optimal pH for different operations during electroplating effluent treatment [2]

Operation	pH
1. Ferric ion oxidation to ferrous state	7
2. Cyanide to cyanate conversion	>10
3. Cyanate decomposition	8.0–8.5
4. Hexavalent chromium reduction to trivalent state	2–3
5. Trivalent chromium precipication	8.5–9.5
6. Copper precipitation	9–10.3
7. Cadmium precipitation	9–12
8. Nickel precipitation	>9.5

[4]Israeli standards.
[5]DRAOT treatment plant specifications.
[6]In most cases, the municipality inspector determines the level on contaminants using test kits. These kits can only detect concentrations above some minimum level: 0.03 mg/li for chromates and 0.1 mg/li for cynanides.
[7]This result was obtained by independent laboratory testing.
[8]Violation caused by plant malfunction.

incorporated into the manufacturing costs just as one includes the costs of handling raw materials.

As in the chemical industry at large, there are three types of effluent temperature processes:

   A. Continuous processes,
   B. Batch processes, and
   C. A combination of the first two.

There is a tendency to consider batch processes as obsolete, primitive and significantly manual labor intensive. However, we believe that this is not true and that the batch process has many significant merits. As a matter of fact, a batch process has been developed for the removal of phosphorous from effluents [1]. We shall now enumerate some of reasons for adopting a batch process for water treatment:

1. The make-up of the different streams form the shop and their flow rates are not constant.
2. The shop operates only on one shift per day, which means that time would be wasted in reestablishing the steady state of a continuous process.
3. There are plans to install additional processes and to modify existing ones.
4. The elimination of the pollutants is controlled by pH and redox potential. Considerable difficulties were experienced in continuous operation and quite often unfavorable (off-specification) results are obtained. Frequently, a considerable amount of substandard effluent will be discharged before laboratory test results are available to indicate problems. In comparison with the frequent laboratory tests that are mandatory for continuous operation, only a single test need be performed for the batch process, usually once a day. Lately, with the availability of inexpensive test kits, effluents from batch processes can now be tested on-site.
5. One of the major potential advantages in favor of continuous processes, smaller equipment size, is lessened as the cost of treatment tanks is relatively low in our case (only 10% of total shop cost).
6. The other draw-back of the batch process, its labor intensive nature, was overcome by implementing computer control. In the case of a failure of the computer control system in a continuous process, one is unable to operate the shop. However, in the case of a batch process, it is quite easy to continue operation in that eventuality under an emergency schedule.
7. In the event of effluent composition (treatment plant feed) changes, it is possible to empirically determine the

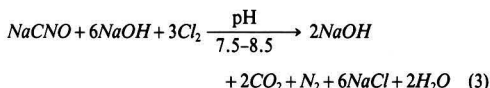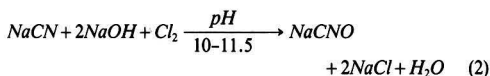new set of operating conditions and then later on to optimize the procedure.

8. Meeting environmental standards has become an essential part of doing business. However, regulations are becoming increasingly tighter. Adjustment of a batch unit to tighter standards is much simpler, especially if the plant has spare capacity. Table 1 presents the present permitted concentrations of metal ions at the plant outlet, at the regional treatment facility and the maximum load.
9. The optimum pH for the precipitation of the heavy metal ions as hydroxides varies according to the ion, as shown in Table 2.
10. The maintenance and cleaning of the equipment of a batch system is easier.
11. The municipal inspector makes periodic visits to the treatment plant to verify that the effluent quality conforms with regulations. Since the batch treatment plant operates off-line, there is always the suspicion that the plant could be discharging untreated effluent. To remove this possibility, a holding tank with a volume equal to the daily discharge was installed as a buffer between the treatment plant and the sewer.

TREATMENT PROCESS

For economic reasons, chemical treatment was selected for both the continuous as well as for the batch systems [2, 3]. The total shop effluent consists of three streams: one containing cyanides, one containing chromates and the acidic and basic streams which contain neither of these two pollutants. In the first stage, the cyanide is removed by alkaline chlorination [4]. The overall reaction is:

$$2NaCN + 8NaOH + 5Cl_2 \rightarrow 10NaCl + 2CO_2 + N_2 + 4H_2O \quad (1)$$

The reaction is actually a two step process. In the first step, the cyanide is converted to cyanate, which is then removed by chlorination in the second step:
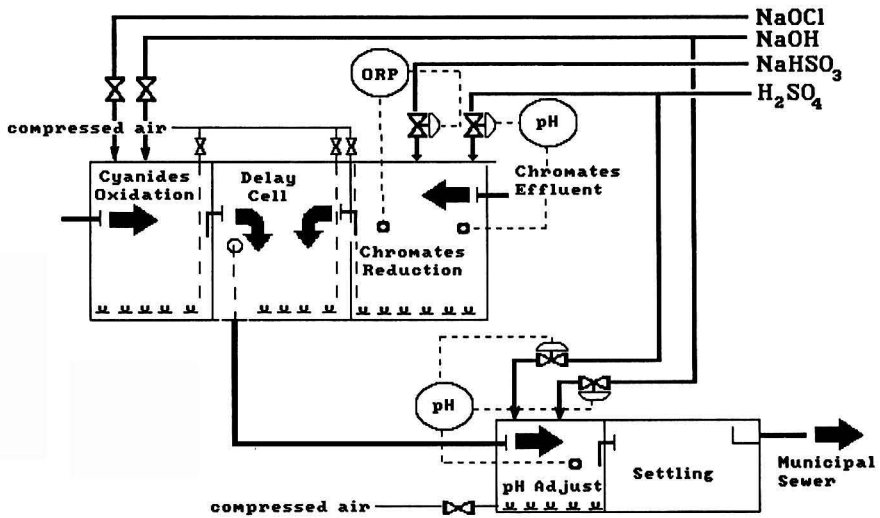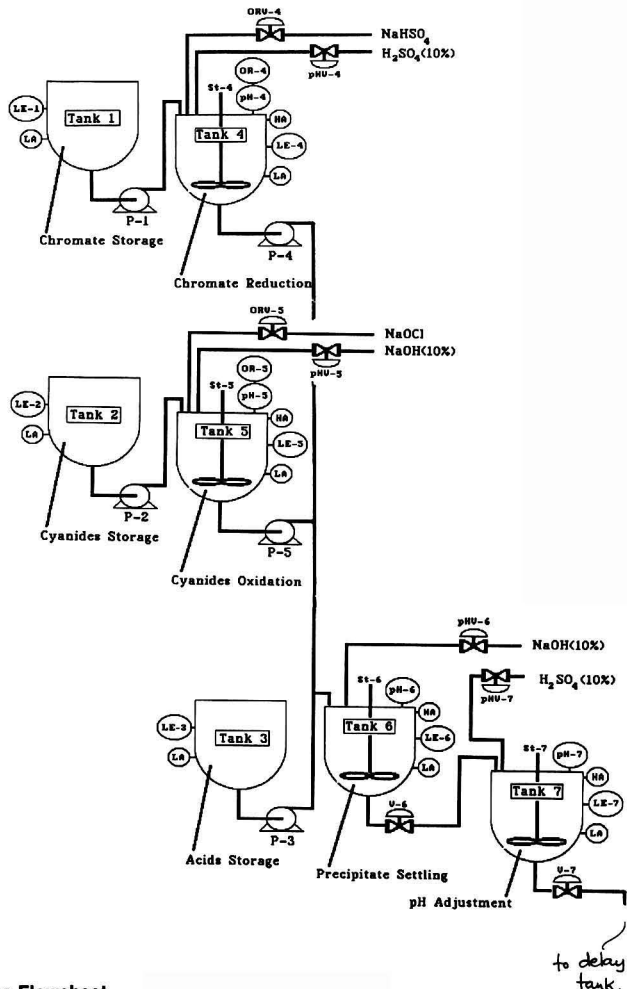
$$NaCN + 2NaOH + Cl_2 \xrightarrow[10-11.5]{pH} NaCNO + 2NaCl + H_2O \quad (2)$$

$$NaCNO + 6NaOH + 3Cl_2 \xrightarrow[7.5-8.5]{pH} 2NaOH + 2CO_2 + N_2 + 6NaCl + 2H_2O \quad (3)$$

FIGURE 1. Continuous Process Flowsheet.

FIGURE 2. Batch Process Flowsheet.

Acid Collection	Chromates Collection	Cyanides Collection
	Charge 15 min.	Charge 15 min.
	Adjust pH=2.6 20 min.	Adjust pH=8.7 35 min.
	Adjust ORP=270mV 40 min.	Adjust ORP=580mV 25 min.
Charge 15 min.	Waiting 10 min.	Waiting 30 min.
	Discharge 15 min.	Discharge 15 min.

Adjust pH=10.5 15 min.

Settling time 120 min.

Transfer time 15 min.

Adjust pH=8.5 30 min.
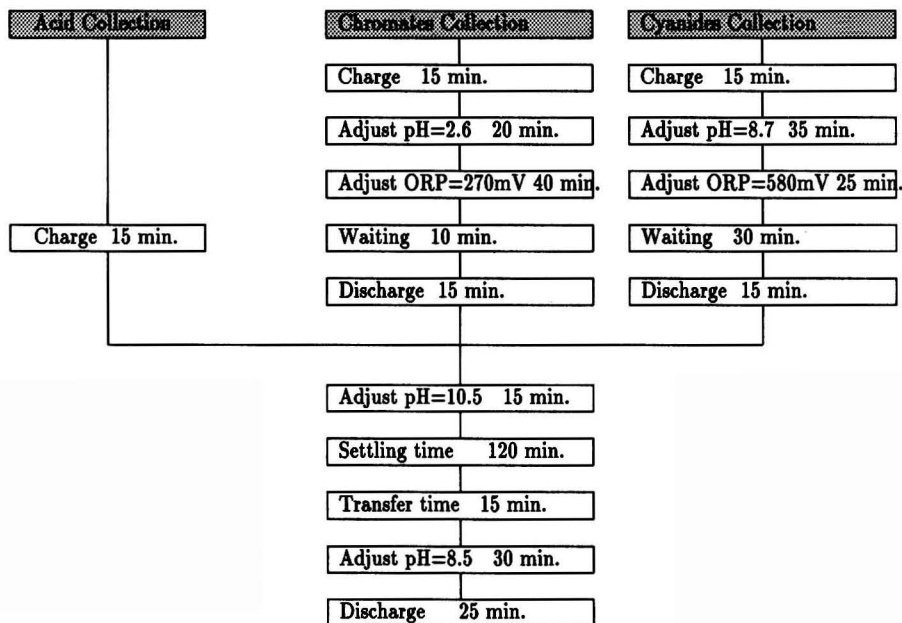
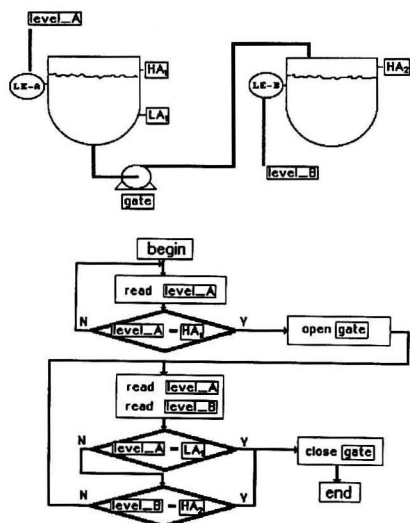Discharge 25 min.

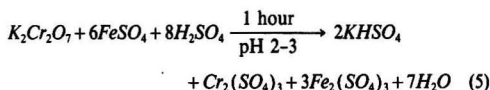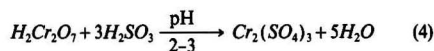**FIGURE 3. Batch Process Sequence Chart.**

FIGURE 4. Logical Diagram for the Operation:
TRANSFER (level_A, level_B, HA₁, LA₁,
**HA₂, gate)**
where level_A is the level of tank A.
   level_B is the level of tank B.
   HA₁ is the high alarm of tank A.
   LA₁ is the low alarm of tank A.
   HA₂ is the high alarm of tank B.
and gate is either a pump or a valve on the line between the the two tanks.

The temperature must be maintained under 50°C at all times in order to prevent the formation of explosive sodium chlorate ($NaClO_3$).

The hexavalent chromium (Cr^{+6}) is reduced to the trivalent state (Cr^{+3}) by treatment using an appropriate chemical-reducing agent:

$$H_2Cr_2O_7 + 3H_2SO_3 \xrightarrow[2-3]{pH} Cr_2(SO_4)_3 + 5H_2O \quad (4)$$

$$K_2Cr_2O_7 + 6FeSO_4 + 8H_2SO_4 \xrightarrow[pH\ 2-3]{1\ hour} 2KHSO_4$$
$$+ Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O \quad (5)$$

The trivalent chromium is precipitated by the addition of sodium hydroxide:

$$Cr_2(SO_4)_3 + 6NaOH \xrightarrow{pH} 2Cr(OH)_{2\downarrow} + 3Na_2SO_4 \quad (6)$$
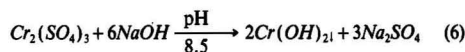
Precipitation of all heavy metals (Cr^{+3}, Cr^{+4}, Ni, Al, Zn, Fe and Cu) is effected by the addition of sodium hydroxide to the wastewater. Finally all three streams are combined and the pH is adjusted to the required level.

Figure 1 shows the flowsheet for the continuous process used at Deutsch Ltd., before the decision to design and erect the batch system. The process flowsheet for the batch system is given in Figure 2. Figure 3 details the sequence of operations involved and the time required to complete treatment. Note that the total holding time in chromate reduction is 100 minutes and the cyanide oxidation is 120 minutes while the settling and pH adjustment section requires 190 minutes. Thus, the treatment of a batch (equal to the effluents of one shift) would be approximately 5 hours, which leaves enough time to allow for possible future changes in the batch process diagram.
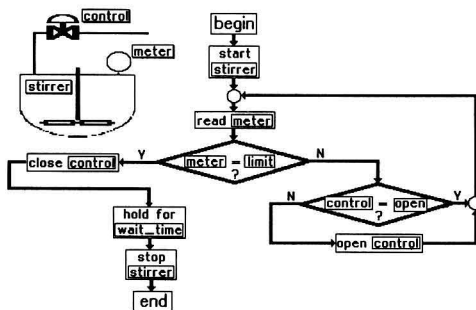
FIGURE 5. Logical Block Diagram for the Operation: QUALITY _ CONTROL (stirrer, meter, limit, control, wait _ time)

where	stirrer	is the agitator of the process tank.
	meter	is a quality indicator returning a value (pH or redox.)
	limit	is a numerical inequality indicating the limit for reaction completion (e.g., "≤250").
	control	is a control valve on a line carrying the chemical control fluid.
	wait_time	is the time for which the operation should remain on hold.

CONTROL SYSTEM

The two basic operations involved: the transfer of fluid from one tank to another, and the control of effluent quality (as indicated by the pH or redox measurement), are computer control modules which can be represented by the logical block diagrams given in Figures 4 and 5. The two operations can be described as follows:

transfer (level_A, level_B, HA₁, LA₁, HA₂, gate²)

In this operation, level_A is continuously read, and gate is opened as soon and level_A reaches the value HA₁. Thereafter either a LA₁ on level_A or a HA₂ on level_B will cause the gate to be closed, thus ending the operation.

quality_control (stirrer, meter, limit³, control, wait_time)

In this operation, stirrer is first activated and then meter is continuously read. If meter reaches limit, the control (valve) is opened. As soon as meter crosses limit, control is closed, the operation goes on hold for wait_time minutes. After that, the stirrer is turned off and the operation is completed.

The control scheme was implemented using Westinghouse's Numa-Logic PC-1100 Programmable Controller. The scheme can be represented by combinations of the basic two building

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[2]here, gate can be either a pump or a valve.

[3]the parameter limit includes a numerical value and associated inequality, e.g., "≥250".

blocks, allowing the entire batch operation to be summarized by the following sequences (level indicators, pH- and redox-meter readings, pump and stirrer numbers as shown in Figure 2):

A.   Chromate Reduction:

transfer (LE-1, LE-4, HA, LA, HA, P-1);
quality_control (St-4, pH-4, "≤2.6", pHV-4, 0);
quality_control (St-4, OR-4, "≤270", ORV-4, 10);
transfer (LE-4, LE-6, HA, LA, HA, P-4);

B.   Cyanates Oxidation:

transfer (LE-2, LE-5, HA, LA, HA, P-2);
quality_control (St-5, pH-5, "≥8.7", pHV-5, 0);
quality_control (St-5, ORP-5, "≥580", ORV-5, 30);
transfer (LE-5, LE-6, HA, LA, HA, P-5);

C.   Loading Acid Waste into Settling Tank:

transfer (LE-3, LE-6, HA, LA, HA, P-3);

D.   Settling Precipitates and pH Adjustment:

if steps A, B and C have been completed:
quality_control (St-6, pH-6, "≥10.5", pHV-6, 120);
transfer (LE-6, LE-7, HA, LA, HA, V-6);
quality_control (St-7, pH-7, "≤8.5", pHV-7, 0);
transfer (LE-7, LE-8, HA, LA, HA, V-7);

As shown in Figure 3, the first three sequences are implemented simultaneously, with the last step carried out only when the first three steps have been completed. As an example, let us look at the cyanates oxidation step in more detail. Cyanidic effluent is collected in Tank 2 which is equipped with high and low level indicators. Upon initiation, Tank 5 is charged using pump P-2. When the waste water in Tank 5 reaches preset level, the pump is shut off and the tanks' pH controller (pH-5) and stirrer (St-5) are activated. The controller maintains pH in the range 8.5–9.0 by actuating a solenoid (pH-5) controlling the flow of sodium hydroxide. When the pH has stabilized in the desired range, the redox controller (OR-5) is activated. The controller is set to the range of 550–600 mV. The redox controller acts on a solenoid valve (ORV-5) which charges sodium hypochlorite. When the oxidation of the cyanides is completed (as indicated by the redox control), the agitation is stopped and all valves are closed. The batch is checked for complete elimination of the cyanides. If the results are unsatisfactory, the oxidation step is repeated. Successful oxidation permits the actuation of pump P-5 in order to transfer of the batch in Tank 5 to Tank 6 for further processing (settling precipitates).

RESULTS

Table 3 shows selected plant data from the Ashdod Municipality inspector's report on the Adar Gilshat Company's treatment plant, which show that spot checks carried out on the

Table 3 Example plant test results from the Ashdod Municipality Inspector's Report

Item	Max. Level	4/10/89	5/23/89	10/12/89	10/25/89
Chromates	0.25 (mg/l)	<0.03[6]	<0.03[6]	0.07	<0.03[6]
Cyanides	2.0 (mg/l)	<0.1[6]	<0.1[6]	<0.1[6]	0.053[7]
pH	6–9	8.0	12.8[8]	7.2	7.9

plant's operation were generally satisfactory. Note the use of test kits to determine ionic concentrations. Some comments are in order. Firstly, one of the main advantages of batch treatment is its capacity to deal with unknown levels of contaminants; thus the measurement of the initial levels of ionic contaminants is neither called for, nor are carried out. Secondly, the results of the tests carried out on the treated effluent are of a "go/no go" nature; either the effluent meets the required specifications and can be safely discharged, or additional treatment must be carried out.

CONCLUSIONS

Circumstances clearly exist favoring a batch process over a continuous one for treating electroplating wastes. Careful design has generated a batch process which utilizes computer control and which performs favorably in comparison to a continuous process while minimizing the manpower requirements.

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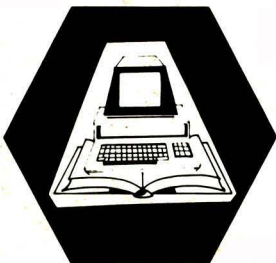**ESL information services**

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