

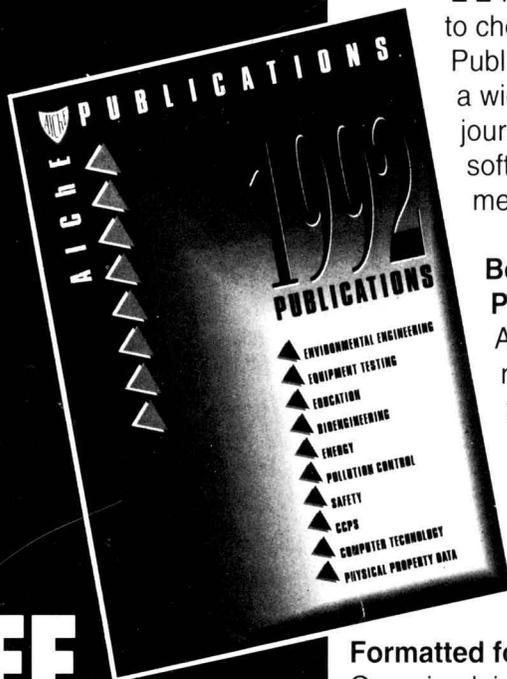
May, 1992

ENVIRONMENTAL PROGRESS



Compliance testing at the MacArthur Waste-to-Energy Facility, Islip, N.Y. Photo courtesy of ETS Inc., Roanoke, VA.

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ENVIRONMENTAL PROGRESS

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

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Waste Avoidance Makes Good Business Sense

Richard D. Siegel, Ph.D

Compliance with the 1990 Clean Air Act Amendments (CAAA) is anticipated to cost this nation's industry \$25 to \$40 billion *per year* by the time the law is fully implemented in 2005. The requirements of the following legislation and regulations add, or will add, equally staggering costs to our already astronomically expensive efforts to return or maintain this good earth to acceptable level of environmental quality for future generations:

- the 1990 Pollution Prevention Act
- OSHA's Accidental Release Regulations
- forthcoming reauthorization of Resource Conservation and Recovery Act (RCRA) and the Clean Water Act (CWA)
- proposed "Right-to-Know-More" legislation, and
- state initiatives such as Massachusetts Toxic Use Reduction Act (TURA) or California's Risk Management and Prevention Program (RMPP)

Furthermore, we know – as surely as our taxes are due every April 15th – new and more stringent legislation will be enacted by the states and the federal government *ad infinitum*.

My fear is that industry will approach compliance with each of the statutes on a piecemeal basis (for example, on the air side: scrubbers, reformulated fuels, fume incinerators, vapor condensers, updated piping and instrumentation diagrams and process flow diagrams). If this happens, some manufacturing facilities will be driven offshore and some companies will be forced entirely out of business. This shift will add to our towering balance of payments deficit.

I am particularly concerned about the effect of these new rules on the chemical industry – one of the few bright spots for America on the international trade level. Can you imagine the impact on batch or toll chemical producers trying to comply with the Environmental Protection Agency's (EPA's) current thinking on the minor modification requirements to their CAAA operating permits as they change formulae or products? Perhaps they'll need to hire a fortune teller to preplan the entire slate of chemicals they will be using and producing. Were I the manager of a chemical plant, the threat of the Department of Justice's (DOJ's) enforcement of the criminal liability provisions of the CAAA for simple paperwork violations would certainly make me consider whether to continue operations at all.

On the upside, these requirements represent an unprecedented opportunity for industry to improve yield, control capital investment costs, focus scarce resources and fulfill its environmental responsibilities in a cost-effective manner that will improve our global competitiveness. In this context, one should think, for example, of an air quality audit not just as a means of demonstrating compliance but as an *opportunity* to redesign a facility, using state-of-the-art systematic design methods to *minimize waste generation at the source*.

With the latest advances in process simulators, it is now possible to include environmental objectives in design criteria by recognizing the true cost of waste and, thus, to retune our processes. After all, if we

- update our processes based on current state of the art technology,
- reduce our raw material losses,
- reduce our end-of-pipe treatment costs,

- reduce yield losses,
- avoid future Superfund or corrective action liabilities,
- conserve water, chemicals and other processes inputs,
- reduce liability from future regulations, and
- reduce our waste disposal costs,

haven't we improved overall process efficiency and yield? Think of this approach as re-optimization of a process at an existing facility based on current process technology or as a design condition for a newly synthesized process starting at the bench. That is, we can optimize the process with respect to a set of criteria that include environmental residuals. By looking at the generation of environmental residuals holistically rather than piecemeal as the laws currently require, one's ultimate cost of compliance can be greatly reduced (for example, try considering the present worth of involvement in a Superfund site).

At our company we are counseling our clients to look at the stringent requirements outlined above, as well as future trends in regulations and legislation, as part of an overall plant design program. We think of this as the ultimate in Total Quality Management. Envision the synergy brought to projects by a team of consulting engineers and scientists that can both keep you in compliance and have the design tools and competence necessary to engineer process solutions, such as maximization of internal recycle. This approach will make you more competitive in the long run.

An example of this thinking, as this editorial is written in mid-April of 1992, is that more than 734 companies have chosen to participate in EPA's 33-50 program aimed at voluntary reduction of 17 toxic chemicals at the source, rather than at end-of-pipe. Their participation, *entirely voluntary* and *unenforced*, gives them a headstart on the anticipated source reduction focus in the pending CWA and RCRA reauthorization bills, potential credit for required CAAA reductions and equally important, the goodwill associated with the public's perception of their good neighbor efforts in this year's Toxic Release Inventory (TRI) reports. This aggressive approach will clearly provide these companies with a major economic asset in their product markets with fewer liabilities in the future.

For American industry to survive as a global competitor in the 21st century, pollution prevention is the ultimate planning tool. Indeed, through the new technologies under development at AIChE's Center for Waste Reduction Technologies (CWRT) and information exchanges with the EPA, we as chemical engineers, have the opportunity to lead the world in this arena and to once again have our nation assume its role as world leader in the international marketplace.

Wherever this idea germinates in a company, the decision to move ahead with the acquisition of this asset ultimately must start in the boardroom, the same place where we're currently debating how to improve our competitiveness. If you believe as I believe, pass the word up the line so that American engineering know-how and ingenuity can lead the changes necessary in our manufacturing processes to permit sustainable growth while concomitantly making our nation and this planet a healthier and better place to live.

*Dr. Richard D. Siegel is Vice President B&V Waste Science and Technology Corp.
100 CambridgePark Drive, Cambridge, MA 02140*

Air & Waste Management Association Call For Papers

An international specialty conference, "The Role of Meteorology in Managing the Environment in the '90s," will be held Jan. 26-29, 1993, in Scottsdale, Ariz. It is cosponsored by the Air & Waste Management Association and the American Meteorological Society.

Papers are invited on the following topics:

- Recent developments in air dispersion modeling (routine and accidental releases)

- Tropospheric/stratospheric ozone issues and modeling deposition and visibility and multi-regional, long-range transport
- Global climate change
- Air monitoring and meteorological field programs
- New developments in meteorological measurements
- Meteorological studies to support RCRA and CERCLA programs
- Forensic meteorology

Send your abstract of 200-300 words by Aug. 1, 1992, to Amiram Roffman, AWD Technologies, 10 Center West, Building 3, Suite 400, Pittsburgh, PA 15276.

The Air & Waste Management Association is a nonprofit environmental education organization with 13,000 members in more than 50 countries. Founded in 1907, the association provides a neutral forum where all sides of an environmental issue receive equal consideration.

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Call for Congressional Action to Improve Management of Industrial Hazardous Waste

Congress "should act this year" to improve the way the nation manages its non-hazardous industrial waste, a chemical industry spokesman recently told a house panel.

Scott Magelssen, speaking for the Chemical Manufacturers Association, said Congress should create a national "framework" through which the states implement their own programs to manage non-hazardous waste. He said it would be a mistake for Congress to duplicate the federal regulatory regime that is currently used to control hazardous wastes.

Industry's volume of non-hazardous waste is "more than 20 times" greater than its volume of hazardous waste, Magelssen told the House Subcommittee on Transportation and Hazardous Waste. The subcommittee is considering an overhaul of the Resource Conservation and Recovery Act (RCRA), the nation's primary waste management law.

"Applying (to non-hazardous waste) a monolithic hazardous waste-like

program, which assumes every waste poses the same risk, would be inappropriate and wasteful," said Magelssen, Assistant Director for Environmental Affairs at Union Carbide Corporation.

Magelssen said that regulatory programs must "deliver the greatest environmental bang for the limited bucks available." He said the existing federal program to manage hazardous waste, "has not been such a program."

He said that while the federal government has focused on hazardous waste in the past 12 years, each of the 50 states have built programs aimed at non-hazardous industrial waste. While the state programs are "not all perfect," Magelssen said, "taken together, they represent a significant investment on which to build a state-based national program."

The federal government, he added, "can play an important role in facilitating, rather than interfering with state programs."

In separate testimony, Larry Bone of

The Dow Chemical Company also appearing on behalf of CMA, said if Congress also decides to address hazardous waste recycling issues in RCRA reauthorization, "it should seek to improve the (current) regulatory regime."

Bone told the House panel that chemical companies currently recycle "millions of tons of materials every year." Since recycling boosts product yield and conserves natural resources, chemical companies "do it everywhere we can," he said.

"Unfortunately," Bone continued, companies "don't recycle as much as they would like to." He said that federal regulations subject many recyclable materials to RCRA's stringent hazardous waste standards. He called these regulations — which require permits that cost up to \$1 million per facility — "obstacles (that) severely discourage industrial recycling of hazardous materials." Bone said that "recycling should not be regulated in the same way as hazardous waste."

Breakthrough in Clean Water Technology Demonstrated at SRS

Researchers at the Savannah River Site have started three new projects to demonstrate better ways to clean solvents out of groundwater and soil using chemical-eating bacteria and natural vegetation.

These activities are part of the U.S. Department of Energy's Integrated Demonstration Project through which DOE laboratories, other government agencies and research organizations are testing the viability of many different technologies for restoring the environment.

Scientists have found that some microbes occurring naturally in groundwater and soil have the ability to completely break down many environmental contaminants. Westinghouse Savannah River Company researchers discovered that injecting methane into the ground and water greatly increases the energy of the microbes to do their work.

According to WSRC scientist Terry Hazen, the new technologies are safer for the environment, very effective, and less costly.

A second microbe project being demonstrated uses a bioreactor a vessel containing the bacteria. The contaminated water is pumped through the vessel and methane is supplied. After treatment the water emerges as drinking water.

Scientists at Oak Ridge National Laboratory, in collaboration with Hazen at the Savannah River Technology Center, have also found that certain vegetation can encourage microorganisms to break down compounds such as solvents.

Washington Environmental Newsletter

Toxic Use Reduction and Use Reporting

As reported in a previous column, AIChE's Washington Representatives are carefully tracking the progress of the provisions for Toxic Use Reduction and Use Reporting (TUR/UR) that have surfaced in RCRA, Clean Water and Right to Know More bills, currently being considered by Congressional Committees. Unlike Pollution Prevention which AIChE strongly supports, TUR provisions seek to ban or drastically reduce toxic chemicals, regardless of their societal benefits, or whether a substitute exists. TUR is based almost solely on a chemicals potential for toxicity, regardless of the amount of its presence in a process or product. These proposals would impact countless numbers of everyday products – motor oil, antifreeze, cosmetics, paints, garbage bags, house siding, roofing, bowling balls, car seats, seat belts, refrigerators, carpets, tires, plastics, furniture, telephones, suntan lotions, pens, and pharmaceuticals will all be affected. Carried to the extreme, a ban on toxic chemical use could severely affect our industries, our ability to develop and produce these products and our position in the global marketplace.

The Right-to-Know-More bill (H.R. 288n) introduced by Representative Sikorski has gained support in the House of Representatives. While H.R. 2880 is described as “just a reporting bill”, it is in effect a broad-based effort requiring EPA to set TUR performance standards for a number of industry categories. It requires the chemical industry to extensively report sensitive, product specific information, thus permitting foreign or domestic competitors to determine the production and process specific data of new products and process technology. These broad based disclosure provisions could provide disincentives for investment in R&D. With more than \$12 billion invested in R&D annually by the chemical industry, H.R. 2880 could have a far reaching impact on our industries and society.

These TUR and UR provisions are of great concern to a large cross section of industrial trade associations, who are now engaged in a massive lobbying effort to modify, weaken or eliminate TUR and UR provisions. Their approach is primarily based on the adverse economic effect that would impact on production and trade.

AIChE's Government Programs Steering Committee (GPSC) is currently preparing commentaries, white papers and briefings that are based on technical and engineering realities, designed to educate lawmakers on chemical use, control and processing knowledge and principles. We believe that a broad ban of toxic chemicals, especially where no effective substitute exists, is a overly simplistic, unrealistic and unenforceable approach to pollution prevention. We strongly support R5cD for source reduction (as evidenced by AIChE's formation of the Center for Waste Reduction Technologies), and R5cD of new recycling, waste treatment and disposal technologies. There is a justifiable need for setting emission standards, but we must make chemical engineering principles and sound technology available to assist lawmakers in their efforts to solve our national pollution problems through workable and realistic approaches. GPSC is also alerting local section GIC's on ways to join in a “grassroots” effort that will enable chemical engineers to be heard on issues that can affect their careers.

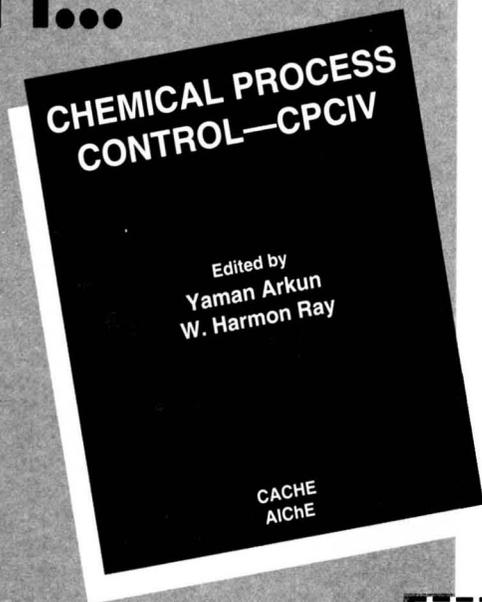
CFC Phase-out Accelerated

The U.S. will phase-out the production of chlorofluorocarbons, halons, carbon tetrachloride and methyl chloroform by December 1995 rather than the deadline of the year 2000 agreed to in the Montreal Protocol. This move comes in the wake of new NASA studies showing that ozone depletion may be progressing more quickly than expected over the Northern Hemisphere.

Because of the impending phase-out of CFC's, substitutes and alternatives for many major CFC uses have been under development for some time. Industry has already cut CFC output by 42 percent since 1986. The President has also called for a reexamination of the schedule for phasing-out ozone depleting CFC substitutes and will consider recent evidence suggesting the need to restrict methyl bromide.

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

PROCESS CONTROL THEORY AND THE CPI...



Despite its advances, process control theory has been slow to realize its full potential in the chemical processing industry. Control experts have “theorized” themselves out of the industrial loop. Control remains mostly an afterthought to process design. Yet safety and economics clearly demand more high-performance, non-linear control techniques in the CPI. Those are among the important issues addressed in the new volume of Chemical Process Control—CPCIV. This 700-page compendium contains 37 of the most significant papers from the Fourth International Conference on Chemical Process Control. It covers virtually every topic in the field that chemical engineers should know about. From inventory control in Japanese plants to modeling in neurobiology, these papers sum up five years of the very latest control applications from industry, academia, and government. This fully indexed volume covers:

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IS THERE A BRIGHTER FUTURE SHINING THROUGH ALL THAT JARGON?

Technology and Politics, M.E. Kraft and N.J. Vig, Duke University Press, Durham, NC, 358 pages [ISBN No.: 0-8223-0846-0] U.S. List Price: \$59.75 – cloth, \$17.95 – paper (1988)

The thesis of *Technology and Politics* is that technology and politics are intertwined, affect each other, and are affected by the actions of each other. The book presents this thesis both from a philosophical and process point of view. It is written by a number of outstanding contributing authors and appears to be carefully edited by Kraft and Vig. The primary thrust of the work is to bring to the fore, by example, how politics and technology interact and in that way impact the human condition.

The work is presented in four sections: (1) Understanding Technology: Philosophy and Politics; (2) Governing Technology: Institutions and Processes; (3) Regulating Technology: Risk Assessment and Management; and (4) Evaluating Technology: Cases and Controversies.

The discussion of Philosophy and Politics and its relation to understanding technology presents chapters written by Norman Vig, Langdon Winner, and Albert Borgmann.

In the first chapter on "Technology, Philosophy, and the State", the author shows how political and social needs affect technology; thus, for example, the decision to market the personal computer, as well as Ford's decision to mass produce an automobile, resulted from the preference for individual freedom and privacy. At the same time, technological advances have affected the political arena because high speed mass communication has altered the electoral process and political awareness.

In the second chapter on "Do Artifacts Have Politics?", Langdon Winner argues that machines can be a "political entity". For example, the development of the large agricultural

machines such as the tomato harvester is both the result of the social order and a symbol that affects different parts of population differently and in that way becomes an active participant in the ebb and flow of social development.

In the section on "Governing Technology", the authors discuss how Presidents can manage technology by the weight they put on programs and the leadership or non-leadership they provide. They discuss how difficult it is to govern technology from the Congressional point of view and why the Office of Technology Assessment was not only developed but how it interrelates to the governance of technology. Allan Mazur in Chapter 7 on "Controversial Technologies in the Mass Media" presents an insightful discussion of how the mass media no longer merely interprets the technology but also shapes it and responds to it.

In this day and age regulating technology is of major concern and major import. In their third group of chapters, the editors present discussions on Risk, Costs, and Benefits. Harvey Brooks discusses the movement toward internalizing the social cost of development and its impact on the rate of innovation. He further discusses the U.S. versus European approach to analyzing risks and controlling risks as a result of technological development. The discussions on analyzing technological risks continue to be germane even though they were presented several years ago.

In the last group of chapters on "Evaluating Technology", a group of case histories is presented. These include discussion of the difficult ethical and policy issues connected with biomedical technology, discussion of evaluating technology through public participation utilizing the nuclear waste disposal controversy as a basis, and lastly a discussion of the scientific adversary procedure.

The editors present "Technology as a

Political Phenomenon". Technology as both a driver and a tool affects our very social fiber and drives political decisions on large technological projects. They believe there is a need for better evaluation of technology, and better and more educated public involvement in that evaluation. They believe that we must envision and anticipate technology's consequences before the effects are manifested and make technology the subject as well as the object of politics.

This book discusses, by example, the very tight connection between technology and politics and it is important that we, as engineers, understand this intertwining and become part of the process that defines the politics that impact technology in addition to being the developers of that technology.

Peter B. Lederman, Ph.D., P.E.
Roy F. Weston Inc.,
Raritan Plaza #1
Fourth Floor
Edison, NJ 08837

Hazardous Waste Site Remediation: The Engineer's Perspective, O'Brien & Gere Engineers, Inc., Robert Bellandi, Technical Editor, Van Nostrand Reinhold, New York, NY, 422 pages, U.S. List Price: \$38.95 (1988).

Two hundred forty million tons of hazardous waste are generated by industry each year in the U.S. A large portion of this waste has historically either not been properly disposed of nor appropriately treated. There are in excess of nearly 20,000 hazardous waste disposal sites in the U.S. This book addresses the issue of investigating, designing, and implementing technology to remediate these hazardous waste sites, from the perspective of a practicing engineer. The book chapters were written by various technical personnel (officer, manager, or senior staff) drawing upon the experience gained from the remediation of

over 100 disposal sites during the past twelve years. Remediation is an environmental challenge since at least one environmental medium has been contaminated by human activities and must be corrected. Each site is unique and different in its characteristics; the technologies involved for the clean-ups are site-specific and vary from one case (and/or location) to another. The text is divided into two major sections, dealing with assessment and remediation.

In the assessment section, chapter 1 summarizes the relevant legislation. Chapter 2 discusses the purpose and execution of field investigations, addressing the history of use at the site, factors of the field investigation, and sampling. Chapter 3 concerns the analysis of hydrogeologic conditions in terms of background information review, non-invasive investigation methods, and invasive field methods, while chapter 4 concerns risk assessment. Chapter 5 addresses the role of the laboratory in remediation work. Chapter 6 concerns itself with health and safety at hazardous waste sites, and chapter 7 involves the use of groundwater models for tracking contaminant migration.

In Section 2 on remediation, chapter 8 begins with the development of a feasibility study by defining objectives, and identifying, scrutinizing, and selecting the most appropriate remediation alternative(s). Chapters 9 through 13 discuss various treatment options available, including such technologies as air stripping, ion exchange, *in-situ* biological degradation, correcting leaking underground storage systems, and incineration. Chapter 14 discusses closure through off-site remedies, while chapter 15 addresses the implementation of remedial measures.

The case histories and "hands-on" experience are valuable assets for this text, providing first-hand knowledge of the treatment technologies and procedures needed in remediation at haz-

ardous waste sites. Although no references were listed after 1986, the reference listing is excellent and provides the reader with the necessary references in

highlighting the authors' points. The book is extremely beneficial in describing the design and implementation of clean-up plans, applying remediation

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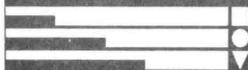
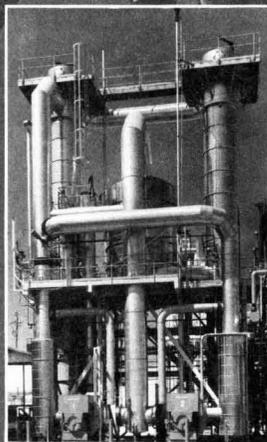
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technologies, describing corrections of leaking underground storage tanks, and describing the collection and analysis of air, water, and soil data. This text should prove to be a valuable asset to those personnel involved in hazardous waste site cleanups, especially environmental and chemical engineers, plant managers, corporate engineers, geohydrologists, government officials, and university students and faculty concerned about the environment.

Robert W. Peters, Ph.D., P.E.,
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Argonne, IL 60439

Right-to-Know and Emergency Planning, George G. Lowry and Robert C. Lowry, Lewis Publishers, Chelsea, Michigan, 421 pages, U.S. List Price: \$ 74.95 (1988)

This easily read book is intended to provide a comprehensive coverage of the necessary information needed to comply with provisions of the Hazard Communication Standard (HCS) and SARA Title III.

The authors provide an excellent survey of considerable information in a moderate level of depth with appropriate references. The target audience includes all affected parties concerned about compliance with provisions of HCS and SARA Title III.

The book is divided into Parts A, B, and C. Part A, which contains three chapters, provides an overview of the need to know the information about chemical hazards along with a summary of the HCS and SARA Title III. Part B contains five chapters which present an excellent discussion of the specific information needed by those parties affected by these laws. Part C contains four chapters which discuss the relationship among the Right-to-Know laws, the affected parties, and other state and

local laws.

The information in this book is presented in a responsible, professional, and logical manner aimed at assisting those parties who have a need to comply with the Right-to-Know laws. This book is an excellent addition to the collection of books dealing with industrial safety and health.

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Control of Emissions from Municipal Solid Waste Incinerators, Pollution Technology Review No. 169, F. Thomas DePaul and Jerry W. Chowder, Noyes Data Corp, Park Ridge, NJ, 275 pages [ISBN No.: 0-8155-1209-0] U.S. List Price: \$ 39.00 (1989)

Disposal of municipal solid waste (MSW) is a national problem. The established practice of landfilling has come under fire because of the short life of existing landfills and the need for siting new ones. Surface and groundwater contamination from leachate from sanitary landfills combined with gaseous emissions have caused a NIMBY syndrome among the public about siting new landfills. Communities are seeking new ways to reduce the volume of waste requiring land disposal. Some communities are turning to waste incineration as an aid to their solid waste management problem. Incineration has the advantages of reducing the volume of material that must be landfilled while recovering energy. The recovered energy can be used to generate steam and/or electricity. Where a market for either exists, incineration is an attractive solid waste management tool. Yet incineration has its environmental drawbacks. In addition to the conventional criteria pollutants, MSW incinerators can emit acid gases, volatile heavy metals, and chlori-

nated organics. All of these must be controlled.

This book, written in 1988, discusses the status of state air toxic programs, incinerator technology, the emissions database, and the available control technologies with their expected effectiveness. The original purpose was for background material for the Illinois Department of Energy and Natural Resources. The book has eight chapters and four appendices. The first chapter is an introduction to the study that provides a justification and overview of the other chapters.

Chapter 2 provides a review of 26 state air toxic programs. Most of these states are east of the Mississippi River with 12 states bordering the Atlantic coast. The states were grouped into three categories depending on how non-criteria pollutants were regulated. Four states had no specific regulations other than those required by EPA and four had comprehensive regulations covering federally regulated and other air toxics. The remaining states have standards for some air toxics with new sources requiring some form of review before a permit is issued. Each state program is discussed separately.

Chapter 3 is a brief review of the combustion characteristics of three general classes of MSW incinerators: mass burn, starved air, and RDF-fired units.

Chapter 4 is an overview of over one hundred references containing emissions data. The uncontrolled emissions data are presented in Appendix A and the controlled emissions data are contained in Appendix B.

The emissions from uncontrolled MSW incinerators are discussed in chapter 5. Statistical analyses of the data in Appendix A are presented in tabular form.

Chapter 6 discusses the various control technologies and combinations that are used with refuse-fired incinerators. Estimated (expected) efficiencies are presented in a table. The importance of

good combustion practices as a means of reducing emissions is stressed. Some discussion is devoted to the impact on emissions by removing certain material from the incinerator feed. This can have significant impact on emissions and incinerator efficiency.

The health risks associated with chemicals that may be emitted from MSW incinerators are given in chapter 7. Unit risk factors developed by the U.S. EPA are combined with the uncontrolled emission factors from chapter 5 to provide a health risk ranking to the various combustors in this study.

Chapter 8 is devoted to the determination of best available control technology (BACT). Each of the combustors is discussed with the estimated capital and operating cost for an emission control system. In each case, a BACT is discussed. Recent BACT determinations for several states are given in Appendix C.

Sampling and analysis methods for the various pollutants discussed in this study are presented in Appendix D.

This book provides a good review of the emissions, health effects, and controls for the three most common types of MSW incinerators. With 146 references, the book provides a good background on the state of municipal waste incineration in 1988. The background section should be useful to any community considering an MSW incinerator as part of their waste management strategy.

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Managing Industrial Hazardous Waste: A Practical Handbook, Gary F. Lindgren, Lewis Publishers, Chelsea, Michigan 48118, 389 pages, U.S. List Price: \$ 59.95 (1989)

The area of hazardous waste manage-

ment is receiving greater attention in industry, due in part to the increasing regulatory requirements. The purpose of this book is to provide those responsible for waste management at manufacturing and industrial firms with a framework to understand the complex regulatory requirements and a philosophy to guide waste management decision making within the regulatory context. A number of examples and practical applications are presented throughout the book.

The text, containing 27 chapters and 11 appendices, is divided into four major sections: I – Basics; II – Regulatory Standards and Responsibilities; III – Developing the Corporate Environmental Management Program; and IV – Selected Considerations in Implementing the Environmental Management Program. Section I, containing five chapters, provides an overview of hazardous waste management systems and it further outlines the regulatory definitions of solid and hazardous wastes. Section II contains nine chapters which provide an in-depth description of the federal regulatory standards applicable to the various hazardous waste generator categories. Section III, which contains seven chapters, presents a philosophical basis for a corporate compliance program. It also provides guidance, and describes the actions and paperwork necessary for such programs. Section IV presents practical information for selecting commercial treatment and disposal vendors, considerations in sampling and analysis, dealing with regulatory agency officials and consultants, legal liabilities, and examples of "best management practices".

The appendices contain examples of some of the commonly used EPA forms, such as the Notification of Hazardous Waste Activity (EPA Form 8700-12) and the Notification for Underground Storage Tanks (EPA Form 7530-1). Also included in the appendices are listing of state hazardous waste manage-

ment agencies, EPA regional waste management offices, commonly used RCRA/CERCLA acronyms and regulatory terms, useful telephone numbers, industrial waste exchanges, DOT Hazard Class Definitions, and examples of potentially incompatible wastes and regulatory requirements for containerized hazardous wastes. The references listed in the bibliography are current and highly relevant to the text discussions.

This book should assist practitioners to establish or modify the company's regulatory compliance program. It focuses on common hazardous waste management activities, such as generation and accumulation or storage of wastes on-site in containers or tanks pending shipment offsite to commercial facilities for treatment and disposal. The book should be very useful for these individuals with manufacturing firms and hazardous waste management responsibilities. This book should be extremely beneficial in establishing a good waste management program at a facility.

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Treatment of Microbial Contaminants in Potable Water Supplies: Technologies and Costs, Pollution Technology Review No. 171, J.T. Troyan and S.P. Hansen, Noyes Data Corporation, Park Ridge, NJ, 335 pages [ISBN No.: 0-8155-1214-7] U.S. List Price: \$ 45.00 (1989)

This book identifies the technologies that are available to inactivating or removing microbial contaminants from drinking waters. The information in the book is compiled from the U.S. Environmental Protection Agency publication entitled *Technologies and Costs for the Treatment of Microbial Potable Water Supplies* by the same authors.

Treatment of Microbial

Contaminants in Potable Water Supplies: Technologies and Costs has as its objective the review of water treatment technologies used by community and noncommunity water systems in removing turbidity, *Giardia*, viruses, and bacteria from water supplies. The book is divided into six chapters, the first of which is an introduction. An Executive Summary is also provided as chapter 1.

Chapter 2 presents background information on waterborne disease outbreaks which have occurred during the latter half of the twentieth century and the problems faced in removing microbial contaminants from water supplies. The latter topic is divided into sections discussing the monitoring of microbial contaminants, using turbidity as an indicator of water quality; and control of bacteria, viruses, *Giardia*, and turbidity. A discussion of alternative approaches to microbial contaminant control is also presented. Forty-seven citations are referenced and ten tables are listed.

In chapter 3, filtration in community systems is discussed. Five filtration technologies are presented: convention; direct filtration; diatomaceous earth; slow sand filtration; and package filtration plants. For each filtration method, the process description and results from laboratory and pilot plant studies are presented. Several case histories are presented. Thirty-six citations are referenced. Nine figures and seven tables are listed.

Disinfection of community water systems is the topic of chapter 4. The chapter is divided into the most applicable and alternative technologies. Chlorination by liquid, gas, hypochlorite, chlorine dioxide, chloramination, and disinfection by ozone are listed as being the most applicable technologies. The alternative technologies discussed include disinfection using iodine, bromine, and ultraviolet irradiation.

Process descriptions and performance, and case histories are presented. Eighty-two citations are referenced. Seven figures and seventeen tables are listed.

In chapter 5, microbial contaminant removal in small water systems (< 1 MGD) is discussed. A brief history of waterborne diseases and treatment facilities, and the difficulties specific to small systems are presented. The remaining portion of the chapter discusses, in greater detail, the technologies used for small systems. Generally, the technologies are the same as those discussed in chapters 3 and 4; however, the emphasis is placed on how these technologies differ when used for small

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water systems. Thirteen citations are referenced. One table is listed.

Cost data for the various processes discussed in chapters 3 through 5 are presented in chapter 6. Costs associated with pumping, chemical feeding, filtration processes, disinfection processes, solids handling processes, and administrative requirements are dealt with separately. In total, this section on cost data accounts for nearly one third of this book. Three citations are referenced. Thirty-seven tables are listed.

In the Appendices, costs associated with groundwater disinfection, obtaining an exemption to the surface water filtration rule, for improving disinfection facilities for operating filtration systems, and regarding land, piping, and finished-water pumping are presented.

Treatment of Microbial Contaminants in Potable Water Supplies: Technologies and Costs provides a good overview on

the methods available for removal of microbial contaminants from surface waters and groundwaters. There is an emphasis on smaller systems. Some material in this book has been obtained from an U.S. EPA manual.

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Hazardous Waste Minimization Handbook, Thomas E. Higgins, Lewis Publishers, Chelsea, Michigan, 250 pages, U.S. List Price: \$ 49.95 (1989)

This is a handbook that would be helpful for a waste minimization program with industrial processes. It is probably the most current book in this field that is on the market today. There are numerous case studies, for example, that lead the reader through "how to do it" exercises in waste minimization.

This book emphasizes economics as the major criteria in determining waste minimization priorities. It covers a variety of industrial processes including metal working, solvent cleaning and degreasing, metal plating and surface finishing, painting and coating, and paint removal. There is also a discussion of waste treatment to minimize the quantity of waste requiring disposal.

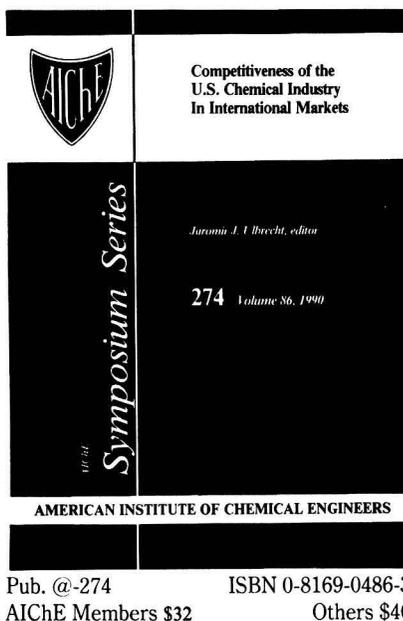
The book is useful in expanding knowledge in the field of hazardous waste minimization. It should be of general interest to managers, operators, and engineers who are involved in the industrial processes that are addressed.

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Environmental Databases

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Introduction

The computer revolution has changed the way we anticipate the future. Knowledge of environmental phenomena, their anticipation, understanding, and prognosis, has increased tremendously with simultaneous advances in computer technology. Industrial growth, now seen to impact the environment deleteriously, is permitted only after assessing its impact on the environment through the use of computing technology or modeling. Environmental management is perhaps the only field where man attempts to write the book of rules without any or with little experience.

Though compliance and remediation are the current focus of environmental agencies, the stress is now on pollution prevention. Now, with powerful computer interfacing, governments all the world over use computers to help predict, prepare for, and respond to a wide range of threats to the environment. Today, computers are huge repositories of information enabling quick access and application in unprecedented environmental episodes or emergencies, and providing sophisticated help in planning and decision making, to avert any catastrophe. Databases play a crucial role in this process. Prediction and/or planning studies, the accuracy of results, possibilities of solution existence, identification of problem areas, documentation of the solutions, report generation, and most of the situations arising typically in air dispersion can be conveniently handled with and due to databases. This review briefly describes popular databases available, their use, and the contact address, to acquire them. The review mainly focuses on those databases available in the air area.

Data Base Management Systems:

With perennial developments, in a rapidly changing field, need of a compatible, flexible and maintainable information system or a database, for regulatory compliance and prevent-

ing pollution, is obviously vital at governmental, organizational, and even international levels, to assist in cost effective record keeping, data acquisition, compliance work, monitoring and so on. The information system strategy will need to include total compliance with environmental regulations, common sharing of data, access of environmental information for those who need to know, capacity for different information systems to exchange data, and a process for auditing the management technology that is available to develop state-of-the-art science systems. Such systems include relational database management software, spreadsheet utility integrated into the DBMS, hypertext and expert systems. Development of such huge databases, to keep abreast with the sweeping move to automate environmental management and data tracking systems thus meeting multifarious needs, has been taken up by governmental agencies and the private sectors. In America itself, 50 to 150 new software, with related databases are developed each year.

It is now widely recognized that corporate well-being and longevity depend on a proactive management of, and response to, volumes of information needed to operate in the new legislative climate. Timely, cost effective compliance and documentation have become critical tools for a well managed environmental program. With exponential growth in environmental laws and regulations, and the punitive impact of non-compliance expected to continue late into the 90's, need to keep current with federal state and local regulations is required to minimize costly corporate risk and liability. Besides legislation tracking, records of operations that affect the environment and their submission to the agencies in proper *proforma* is an added responsibility of environmental managers. Under terms of the Clean Air Act, permits are issued on the basis of regular monitoring, testing and record keeping of emissions. Thus, all the above problems can be smoothed by adopting automation in environmental information rather than persisting with manual systems. Problems like air permits, spills, emergency response programs, regulatory compliance, prevention and its short and long term cost effective-

ness, violation types, monitoring data, process design improvements, material substitutions and a host of other paraphernalia can be managed using a good database information management system.

For such versatile use, the moot issue in large corporations, or governmental agencies is whether to build, or buy such a tailor-made, situation specific system. Other problems include its cost, user independence, ability of updating and modifying, training and technical support. The rule of the thumb is that if a system meets 50% of an organization's need, the best course is to buy it and modify it. Thus, well designed data acquisition and management software has become an essential business tool in the 90s. To provide standardized credible databases in this sector, the federal agencies have undertaken the task of developing, upgrading and offering free of charge or at a nominal fee, basic scientific databases required in regulatory and modeling work, and a host of regulatory and statistical databases. The private sector either develops user friendly, multi-functional databases customized for each company, or it makes governmental databases user friendly and markets these modified databases. Evaluation of any database is thus imperative before choosing it as the required DBMS. Yet, the sheer volume of competitive packages in the field make evaluation a very daunting task. Some of the basic parameters needing consideration to choose a data management information system include:

- a) Analysis of needs, present and future. Priorities of needs should be decided upon.
- b) Experience and past record of the vendor.
- c) Compatibility of the information system with existing and planned software.
- d) Ability to customize the software to special requirements if any.
- e) Expandability and flexibility in terms of future expansions, user changes, and upgradations.
- f) Ease of use and understanding.
- g) Availability of training, and on-line technical assistance and support.
- h) Costs involved.
- i) Multiuser multilocation network formation ability.

Depending on how each parameter weighs, decisions regarding information system acquisitions should be made.

Reviewing the concurrent databases in the industry, like the burdens of Sisyphus, is a never-ending story. New, upgraded databases are found to replace older ones at a rapid pace and with greatly enhanced features. Some of the databases are developed by the Environmental Protection Agency (EPA) as a feature offered by their Information Systems Inventory that consists of more than 600 EPA systems, databases and models. Many of these are provided to the public free of charge or at a nominal on-line user fee. A review of existing EPA data-

bases on air and related areas and other agency and commercial databases follows. This is the first one of a subsequent series of such reviews to come in an endeavor to keep abreast with the software scenario.

The available databases [1,2,3] are in tabular form and classified in the following manner:

- 1) Air related Databases: In Table 1, all the databases are those addressing basic air pollution modeling, heavy and flue gas dispersion and other problems related to the transport physics of air pollutants.
- 2) Physical/Chemical databases: These databases, shown in Table 2, discuss the chemical and physical attributes of various toxic and hazardous pollutants. They also describe heavy gas dispersion, storage tank emissions and the applicable legislation.
- 3) Miscellaneous databases: As shown in Table 3, these databases address all regulatory requirements of the Clean Air Act (CAA), the Superfund Amendments And Regulations (SARA) title III, and they also address the publications in these fields.

The classification used here is on an *ad-hoc* basis. The idea is to introduce the reader to the importance of databases, the selection process involved in a database, and the basic types of databases available in the air pollution area. The classification aims at highlighting the basic purpose and function of available databases.

Conclusion

Not all the databases from the air area available currently are introduced in this review, considering the restrictions of space. Besides, the rate at which new and better databases are introduced or the older ones reintroduced with enhanced features is quite stupendous. A number of databases are now available to assist investigations involved in environmental impact studies. These databases are applicable even to university research. It is hoped that these databases will be of use in the readers' research or business endeavors.

References

1. Kokoszka, L. C., "Guide to Federal Environmental Databases", Pollution Engineering, pp 83-92, Feb 1992.
2. Rich, G., "Picking Environmental Software", Pollution Engineering, pp 46-66, Jan 1992.
3. "Computers: tools for environmental management in the industry-part I,II", Industry and Environment, UNEP, Vol. 14 Nos. 2 & 3, July-Sept 1991.

Table 1 - Air-Related Databases

<u>Database Name</u>	<u>Description</u>	<u>Contact Agency</u>
1) AIRS (Aerometric Information Retrieval System)	This consists of information about air-borne pollution in the U.S. It is divided into four subsystems: AQS, AFS, AMS and GCS.	U.S. EPA (MD-14) Research Triangle Park, NC 27711 Telephone: (919) 541-5456
2) The Applied Environmental Meteorological Tables	It provides meteorologists and others who use meteorological information with definitive data they need in a tabular format. Besides regular atmospheric variables it gives geodetic tables, solar movement Blackbody radiation, particle viscosities Sound speed, moist air variables and fire weather tables.	Dr. Tom Beer Principal Research Scientist Commonwealth Scientific and Industrial Research Organization (CSIRO) Australia.
3) BATEX (Bouffes Atmospheriques Toxiques Explosives)	Used in assessing the impact from accidental releases of toxic chemicals to the atmosphere.	J.P. Degrange CEPN, B.P. 48 92263 Fontanay-aux-Roses Cedex, France Telephone: 33 1 46 54 76 60
4) BEE-LINE Software	Meteorological data can be fed upgraded and accessed for dispersion calculations.	Rod Truesdell Meteorologist Bowman Environmental Engineering P.O. Box 29072 Dallas, TX 75229 Telephone: (214) 241-1895
5) EFFECTS	Used for hazard identification. Contains a hazardous substance databank.	J.M. Blom-Buruggeman MT-TNO Dept., of Industrial Safety Netherlands Organization for Applied and Scientific Research P.O. Box 342, 7300 AH Apeldoorn The Netherlands Telephone: (31) (55) 49 34 93

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Table 1. Continued from previous page)

<u>Database Name</u>	<u>Description</u>	<u>Contact Agency</u>
6) FACTS (Failure and Accident Technical Information System)	Contains information on 15,000 industrial accidents worldwide with hazardous materials. It generates accident reports and case histories, accident abstracts etc.	B. van Beek, DB Manager TNO, Netherlands Organization for Applied and Scientific Research P.O. Box 342, 7300 AH Apeldoorn, The Netherlands. Telephone: (31) (55) 49 38 10
7) FGDIS (Flue Gas Desulfurization Information System)	Describes and identifies boilers and their associated flue gas desulfurization systems.	James Kelly Department of Energy Telephone: (202) 586-8420
8) IRIMS (the Ispra Risk Management Support System)	The system integrates a number of databases containing information relevant to risk management.	Dr. P. Haastrup Acting Sector Head Commission of the European Communities Joint Research Center ISPRA 21020 ISPRA (VA) Italy Telephone (39) (332) 789 603
9) Historic Sulfur Dioxide and Nitrous Oxide emissions estimates	It deals with the results of comparison of historic emission data sets. Available in diskette form.	U.S. National Technical Information Service Department of Commerce 5285 Port Royal Road Springfield, VA 22161 Telephone: (703) 487-4650
10) MHIDAS (The Major Hazard Incident Data Service)	It establishes a data base of major incidents that could be used for validating assumptions and judgements in safety assessment.	A. Harding, DB Manager SRD Wigshaw lane Culcheth, Warrington WA3 4NE Cheshire, UK Telephone (44) (925) 232000 ext. 4486

(Continued on following page)

(Table 1 Continued from previous page)

<u>Database Name</u>	<u>Description</u>	<u>Contact Agency</u>
11) NAVOC (National Ambient Volatile Organic Compounds Database)	175,000 records consisting of the ambient measurements, indoor data, and data collected with personal monitors for about 320 VOC's are compiled and critically evaluated.	U.S. National Technical Information Service Department of Commerce 5285 Port Royal Road Springfield, VA 22161 Telephone: (703) 487-4650
12) NATICH (National Air Toxics Information Clearinghouse)	This Database contains information on the air pollution control agencies and citation/abstracts from the NIOSH, EPA and other agency publications.	The Clearinghouse Staff Pollutant Assessment Branch MD-13 U.S. EPA Research Triangle Park, NC 27711 Telephone: (703) 487-4650
13) SAROAD (Storage and Retrieval of Acrometric Data)	This system assists in editing, storing, summarizing, and reporting ambient air quality data.	U.S. EPA (MD-14) Research Triangle Park, NC 27711. Telephone (919) 541-5456

Table 2 Physical/Chemical Databases

<u>Database Name</u>	<u>Description</u>	<u>Contact Agency</u>
1) CHEMEST	It is an enhanced version (2.0) of the database for toxics and vapor cloud-forming chemicals.	Arthur D. Little Inc. 20, Acorn Park Cambridge, MA 02140-2390 Telephone: (617) 864-5770 ext. 5000
2) CASR (Chemical Activity Status Reports)	The database lists chemicals studied by the EPA in the course of regulatory or research activities.	Chemical Info. Systems Inc., 7215 York Road Baltimore, MD 21212 Telephone: (301) 321-8440

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(Table 2. Continued from previous page)

<u>Database Name</u>	<u>Description</u>	<u>Contact Agency</u>
3) Chemcalc 1: Separation Calculations Chemcalc 17: Chemical Compound Database Thermosim 1: Equil	These databases enable quick EPA storage tank emissions according to EPA publication AP42. The databases also search for user prompted hazardous material and retrieve information on 1,400 compounds.	Gulf Publishing Co., P.O. Box 2608 Houston, TX 77252-2608 Telephone: (713) 520-4438
4) CHEMSAFE	It supplies recommended fire and explosion safety values. It contains critical evaluated physico-chemical properties for about 1,350 chemical properties, fire and explosion hazards, plus a lot of other information.	Dr. R. Eckerman HOD Information Systems and Databanks DECHMA Theodore-Heuss-Alle 25 D-600 Frankfurt 97 Germany.
5) Chemtox Database	As the name suggests this is a database of chemicals and their properties, especially the toxic chemicals.	Van Nostrans Reinhold [2]
6) CIData	Basically this is a database on the regulations of the CAA, as applicable to hazardous and toxic chemicals drawing on its chemical database to generate regulatory procedures.	HazMat Control Systems 3409 Lakewood Boulevard Suite 2C Long Beach, CA 90908 Telephone: (213) 429-9055
7) EIS and EIS/C (Emergency Information System)	Comes with a variety of capabilities like graphical display, mapping, related to pre-loaded 2600, and user entered chemicals.	Joseph S. Applebaum Chemical Emergency Management Specialist Research Alternatives Inc. 966 Hungerford Drive - Suite 1 Rockville, MD 20850

(Continued on following page)

(Table 2. Continued from previous page)

<u>Database Name</u>	<u>Description</u>	<u>Contact Agency</u>
8) Enflex Info	Equipped with the requisite databases (Enflex Data). Enflex Info is an environmental regulatory information system consisting of 16 modules describing facilities, chemical inventory, permit tracking, container tracking SARA 313 form R, using whatever state, local and federal agency reports that can be generated.	ERM Computer Services 855 Springdale Drive Exton, PA 19341 (Telephone: 1-800-544-3118)
9) EnviroFate (Environmental Fate Database). It consists of six interrelated files. a) BIOLOG (Microbial Degradation/Toxicity Data) b) CASLIST (Chemical Name File) c) Chemfate (Chemical Name File) d) DATALOG (Environmental Fate Data) e) XREF (Journal Citations) f) BIODEG (Value Biodegradation file).	A relatively exhaustive database useful for describing the fate or behavior (transport and degradation) of chemicals released in the environment. Environmental transformation rates coupled with physical/chemical properties can be accessed through it. Several thousand chemicals are listed.	U.S. National Technical Information Service Department of Commerce 5285 Port Royal Road Springfield, VA 22161 Telephone: (703) 487-4650
10) Envirofate ISHOW Merck Online	These are chemical databases used for the dispersion of heavy gases and for modeling toxic release scenarios.	Chem Milti Base [2]
11) Gasprops Hycarb	This is a database which accounts for the varied properties types and applications of a large number of gases and compounds from the hydrocarbon families.	Software Systems Corp., [2]

(Continued on following page)

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(Table 2. Continued from previous page)

<u>Database Name</u>	<u>Description</u>	<u>Contact Agency</u>
12) IFIS (Industry File Index System)	This collects EPA regulations on particular industries and chemicals. The database has features of search through industry or through chemical names etc.	Chemical Info, Systems Inc., 7215 York Road Baltimore, MD 21212 Telephone: (301) 321-8440
13) MIDAS (the Meteorological Information and Dispersion Assessment System)	It allows mapping, modeling for 80 preload and up to 120 user entered chemicals. Its application is in planning and implementation of emergency response, and for real life assessment of the effects of chemical spills.	Keith Woodward PLG 1615 M Street N.W. Washington, D.C. 20036 Telephone: (202) 659-1122
14) RIB (the Rescue Services Info. Bank)	Computerized data of hazardous substances, useful for planning all kinds of fire and rescue operations, planning, prevention and response.	B. Albinson National Rescue Services Board Statens Raddningsverk Norra Klaragatan 18 Karolinene S-65180 Karlstad, Sewden Telephone: (46) (54) 10 43 7015)
15) Site Wach	This is an extensive compilation of hydrocarbons, gases, chemicals, and regulations to give a monitoring capability of equipment over a 100 site remediation locations.	Enviralert Inc., 1215 North Tustin Avenue Anaheim, CA 92807 Telephone: (714) 632-3525

Table 3 Miscellaneous Databases

<u>Database Name</u>	<u>Description</u>	<u>Contact Agency</u>
1) CAMEO II (Computer Aided Management of Emergency Operations)	It is conveniently designed to allow user access to vital information about the material during an emergency. It can dial CHEMTREC (The Chemical Transport Emergency Center)	National Safety Council 444 North Michigan Avenue Chicago, IL 60611

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Software Review

(Table 3. Continued from previous page)

Database Name	Description	Contact Agency
2) CARD (Contractor Laboratory Analytical Results Database)	Serves as the quality assurance database for the Superfund Contract Laboratory Program. It includes QA/QC parameters for organic, inorganic and dioxin samples.	Mike Carter U.S. EPA 401 M Street S.W. Washington, D.C. 20460 Telephone: (202) 382-7909
3) ERNS (Emergency Response Notification System)	This is a national database used to collect information on oil and hazardous substances.	Robert Walter U.S. DOT Transportation System Center Cambridge, MA Telephone: (617) 494-2626
4) FINDS (Faculty Index System)	This is an automated inventory of sites and facilities regulated by the EPA. FINDS records the names, addresses, other locational data, and a reference to the responsible agency program office.	Dan Cirilli FINDS System manager U.S. EPA Telephone: (202) 382-2416
5) HACS (Hazardous Assessment Computer System)	This stores detailed hazard evaluation information available to on-scene coordinators.	Chemical Substance Information Network 1300 N. 17th Street Arlington, VA 22209
6) NIOSHTIC	This is NIOSH's computerized bibliographic occupational and health safety database. It contains 110,000 articles from over 150 journals.	DIALOG Info. Services 3460 Hillview Avenue Palp Alto, CA 94304
7) RTECS	Developed by the NIOSH, it contains toxic effects data on more than 100,000 chemicals including irritation, carcinogenicity, mutagenicity, and reproductive consequences.	Chemical Info. Systems Inc., 7215 York Road Baltimore, MD 21212 Telephone: (301) 321-8440

(Continued on following page)

Software Review

(Table 3. Continued from previous page)

<u>Database Name</u>	<u>Description</u>	<u>Contact Agency</u>
8) SKIM	This is an inventory of equipment available for pollution abatement.	National Response Center Telephone 1-800-424-8802
(9)Historic Sulfur Dioxide and Nitrous Oxide emissions estimates	It deals with the results of comparison of historic emission data sets. Available in diskette form.	U.S. National Technical Information Service Department of Commerce 5285 Port Royal Road Springfield, VA 22161 Telephone: (703) 487-4650
10) MHIDAS (The Major Hazard Incident Data Service)	It establishes a data base of major incidents that could be used for validating assumptions and judgements in safety assessment.	A. Harding, DB Manager SRD Wigshaw Lane Culcheth Warrington WA3 4NR Cheshire, UK Telephone: (44) (925) 232000 ext. 4486
11) NAVOC (National Ambient Volatile Organic Compounds Database)	175,000 records consisting of the ambient measurements, indoor data, and data collected with personal monitors for about 320 VOC's are compiled and critically evaluated.	U.S. National Technical Information Service Department of Commerce 5285 Port Royal Road Springfield, VA 22161 Telephone: (703) 407-4650
12) NATICH (National Air Toxics Information Clearinghouse)	This database contains information on the air pollution control agencies and citations/abstracts from the NIOCH, -EPA and other agency publications.	The Clearinghouse Staff Pollutant Assessment Branch MD-13 U.S. EPA RTP, NC 27711 Telephone: (919) 541-0850
13) SAROAD (Storage and Retrieval of Aerometric Data).	This system assists in editing storing, summarizing, and reporting ambient air quality data.	U.S. EPA MD-14 RTP, NC 27711 Telephone: (919) 541-5433

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Integration of RCRA Corrective Action with Clean Water Act Compliance

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A synthetic fibers manufacturing facility is implementing an integrated phased program to upgrade its existing wastewater treatment plant (WWTP) to comply with both the Clean Water Act and the Resource Conservation and Recovery Act (RCRA). The existing WWTP consists of an influent settling basin, two equalization basins, two aeration basins with low- and high-speed aerators, three secondary clarifiers, post-aeration, and belt filter press dewatering with on-site landfilling. The existing WWTP will be replaced with a tank-based system that will include equalization, biological treatment, clarification, effluent filtration, and effluent diffusion. RCRA regulatory compliance incorporated the Corrective Action Program, the Toxicity Characteristic Rule, the Land Disposal Restrictions, and closure/postclosure requirements. Clean Water Act compliance incorporated the Organic Chemicals, Plastics, and Synthetic Fibers (OCPSF) effluent guidelines, effluent toxicity, and general water quality requirements. Logistically, project implementation involved fast-track design and construction, close regulatory interface, and maintenance of production process continuity.

Introduction

This synthetic fibers manufacturing facility, located in the southeastern United States, is implementing an integrated phased program to upgrade its existing wastewater treatment plant (WWTP) to comply with both the Clean Water Act and the Resource Conservation and Recovery Act (RCRA).

The existing WWTP consists of an influent settling basin, two equalization basins, two aeration basins with low- and high-speed surface aerators, three secondary clarifiers, post-aeration, and belt filter press dewatering with on-site dewatered sludge landfilling. The five basins are unlined, incised surface impoundments. Figure 1 illustrates the existing WWTP.

In 1987, the existing WWTP was identified as a solid waste management unit (SWMU) under RCRA jurisdiction. In 1990, the process wastewater was defined as hazardous under the Toxicity Characteristic (TC) Rule. The settling basin never received TC wastes; therefore, it must be remediated under RCRA Corrective Action Program authority while the equalization and aeration basins fall under more restrictive RCRA authority. The remaining WWTP unit processes are components of the SWMU but do not have specific RCRA implications.

In 1988, the new effluent guidelines for the Organic Chemicals, Plastics, and Synthetic Fibers (OCPSF) subcategory were finalized. These regulations established significantly more stringent effluent limits for biochemical oxygen demand (BOD), total suspended solids (TSS), and pri-

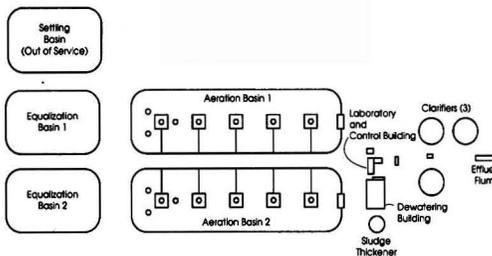


FIGURE 1. Existing wastewater treatment plant.

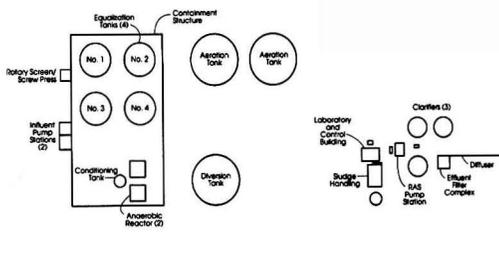


FIGURE 2. Future wastewater treatment plants.

ority pollutants.

The existing WWTP was constructed in phases, starting in the 1960s. As National Pollutant Discharge Elimination System (NPDES) permit limits became more restrictive, unit processes were added to improve performance. With the combination of the recent RCRA and Clean Water Act regulations that impact the WWTP, major modifications were imminent.

A phased program to upgrade the WWTP was initiated in 1988 and includes:

1. Preliminary treatment consisting of influent pumping, screening, dewatering, and equalization to replace the existing settling and equalization basins.
2. Biological treatment consisting of tank-based two-stage anaerobic/aerobic or single-stage aerobic treatment to replace the existing aeration basins.
3. Clarifier modifications to improve unit process performance.
4. Effluent filtration and diffusion to improve effluent quality and comply with toxicity requirements.

These modifications will be completed in early 1993. Figure 2 illustrates the layout of the future WWTP after construction is complete.

The future WWTP will be constructed in the same general area as the existing WWTP. To accomplish this, existing unit processes will be decommissioned and new structures will be constructed in their place. This will require closely coordinated construction sequencing. The program to upgrade the existing WWTP integrates current and foreseeable future regulatory compliance criteria into all aspects of the process selection, design, construction, and operation of the future WWTP. The integration strategy addresses regulatory compliance, regulatory-driven schedule constraints, multiple agency jurisdiction and authority, and production and WWTP process continuity.

Regulatory Compliance Challenges

Resource Conservation and Recovery Act

Once the WWTP was designated an SWMU under RCRA, closure was complicated by the potential presence of past releases of hazardous wastes and/or hazardous con-

stituents (40 CFR Part 261) into the environment. The WWTP unit processes that accepted a designated hazardous waste became RCRA regulated management units (RMUs). For hazardous wastes under RCRA, treatment standards are established for minimum treatment technology requirements to allow continued operation. When these requirements cannot be met, then the RMUs must be closed under the closure and/or postclosure permit requirements. The normal complexities associated with design and construction of the future WWTP would escalate if RCRA requirements for decommissioning the existing WWTP and underlying soils prior to construction of the new system were triggered.

Under RCRA authority, several regulatory issues can apply to closure of the existing WWTP:

1. RCRA Corrective Action.
2. TC Rule.
3. Land Disposal Restrictions (LDR).
4. RCRA Closure and Postclosure Requirements.

Corrective Action Program

The Hazardous and Solid Waste Amendments (HSWA) of 1984 (Section 3004(u)) instituted the regulatory authority to address corrective action for releases of hazardous waste or hazardous constituents from any SWMU at the facility. On July 27, 1990, regulations ("Corrective Action for Solid Waste Management Units at Hazardous Waste Management Facilities") were proposed (40 CFR 264, Subpart S) to establish a comprehensive regulatory framework for implementing the RCRA Corrective Action Program. Regulatory agencies (both state and federal) are initiating activities as if this were the final rule. The RCRA corrective action process typically involves the RCRA Facility Assessment (RFA), RCRA Facility Investigation (RFI), Corrective Measures Study (CMS), and Corrective Measures Implementation (CMI). At any time in this process, interim measures (IMs) may be initiated.

An RFA was conducted at this manufacturing facility in 1987 by the state and federal agencies. 14 SWMUs (including the WWTP) were identified. Concurrently, a Part B post-closure permit application was submitted for three of the identified SWMUs. One of the postclosure permit conditions issued in 1989 required an RFI at eight of the SWMUs. The

existing WWTP was identified as a single SWMU and is currently undergoing groundwater sampling and analysis as part of the initial RFI. The final RFI work plan has been prepared and was submitted to the state and federal agencies for review in 1989. Approval (after adjudication of review comments) is anticipated in the first quarter of 1991.

Toxicity Characteristic Rule

The TC Rule was published by EPA in March 1990 and was subsequently adopted by the state. When this rule became effective on September 25, 1990, this facility's process wastewater became a TC hazardous waste under RCRA due to the presence of benzene. As a result, the WWTP surface impoundments (equalization and aeration basins) receiving process wastewater after this effective date became RMUs. A Part A permit and a modification to the facility's existing Part B permit were submitted to include the newly designated RCRA surface impoundments (defined in 40 CFR Part 264.90).

The settling basin was taken out of service prior to the effective date of the TC rule, so it did not become a regulated unit requiring formal RCRA closure, although it remains in the RCRA Corrective Action Program. In the preamble to the proposed Subpart S rule, voluntary cleanup consistent with EPA cleanup goals is encouraged. To integrate the settling basin into the WWTP modification program, remediation of this SWMU was proposed as an IM under the RCRA Corrective Action Program as described previously.

Land Disposal Restrictions

The "third-third" of the LDR was finalized on May 8, 1990. The LDRs establish treatment standards for land disposal units (that is, surface impoundments). Land disposal units that receive wastes with hazardous constituents exceeding the treatment standards must meet RCRA minimum technology requirements or they cannot be used. The actual date for promulgating treatment standards for TC wastes has not yet been finalized; however, proposed treatment standards are anticipated in March 1992 and final standards are expected in April 1993. The TC Rule requires that all surface impoundments not meeting RCRA minimum technology requirements be closed no later than March 1994. Therefore, the five existing WWTP surface impoundments may have to be closed as early as April 1993 but no later than March 1994. Because of the significant impact of the treatment standards, the April 1993 deadline was selected as the target deadline and is the key regulatory-driven deadline for this project.

Closure and Postclosure Requirements

The settling basin is currently being remediated as an IM under the RCRA Corrective Action Program due to its designation as an SWMU. This remediation includes removing all

sludges from the settling basin for disposal in the on-site landfill, sampling and analysis of exposed soil to assess the nature and extent of any contamination, and backfilling the impoundment with clean soil. Groundwater remediation, if necessary, will be addressed by the RFI and CMS.

The equalization and aeration basins will be closed in a technically similar approach but under 40 CFR Part 264/265 Subparts G and H due to their designation as RMUs. Because the equalization and aeration basins were originally being addressed as SWMUs under the already initiated corrective action program, and have more recently become RMUs requiring closure according to 264/265 closure performance standards, closure is complicated from a regulatory standpoint. Complications are also accentuated because these closure activities are an integral part of the new WWTP modification program.

Closure plans for the four RMU surface impoundments include the removal of contaminated soils exceeding action levels so that contingent closure as a landfill and postclosure care would not be required. Soil sampling and analysis will be conducted to confirm that action levels are not exceeded or that no further remediation is necessary. As with the settling basin (SWMU), it has been proposed that groundwater contamination be addressed in the RFI under the corrective action program.

Efficient closure of the SWMU and RMU surface impoundments (that is, soil sampling conducted one time only) is critical to the timely implementation of the WWTP modifications due to the phased construction schedule. Any delays that result from difficulties in certifying closure under RCRA of each surface impoundment will jeopardize the existing construction schedule.

Sludge and soils from the surface impoundments are currently planned to be disposed of in the on-site permitted industrial waste landfill. Sampling and analysis to verify that these materials are not TC hazardous wastes will be conducted prior to excavation. If they are determined to be hazardous, then closure complications will arise. Transportation to and disposal at a certified off-site commercial RCRA hazardous waste treatment storage and disposal facility (landfill) will have to be implemented if the sludge and soil are found to be hazardous. If the LDR treatment standards for TC hazardous wastes are promulgated, then hazardous waste excavation and disposal will have to be carefully managed so as not to trigger prohibitions on "placement" of restricted wastes.

Clean Water Act

The WWTP is presently operating under an NPDES permit which expires in September 1991. As a result of the Clean Water Act Amendments of 1987, the new NPDES permit must incorporate:

1. OCPSF effluent guidelines.
2. Effluent toxicity limits.
3. General water quality requirements.

Table 1 - Current and Estimated Future NPDES Permit Limits

Parameter		Limits (mg/l)	
		Current	Future
BOD	Average Day	110/146 ^a	25
	Maximum Day	220/275 ^a	60
TSS	Average Day	101	40
	Maximum Day	250	119
NH ₃ -N	Average Day	2	-
	Maximum Day	4	-
PO ₄ -P	Maximum Day	26	26
pH (S.U.)	Maximum Day	6-8.5	6-8.5
DO		5.0	5.0

^aSummer/winter limits

The OCPSF effluent guidelines establish limits for BOD, TSS, and priority pollutants that will be significantly more stringent than the current limits. Average day winter and summer BOD limits will be reduced from 146 and 110 mg/l, respectively, to approximately 25 mg/l. Similarly, maximum day limits will be reduced from winter and summer limits of 275 and 220 mg/l, respectively, to approximately 60 mg/l. Current average day and maximum day TSS limits will be reduced from 101 and 250 mg/l, respectively, to 40 and 119 mg/l, respectively. The current permit includes limits for ammonia nitrogen; however, the OCPSF guidelines for BOD include the nitrogenous demand so the ammonia limit may be negotiated out of the permit. Table 1 presents both the current and estimated future NPDES permit limits.

State regulations require acute toxicity testing when WWTP flows are between zero and 10 percent of the receiving stream's 7Q10 (average low flow for seven consecutive days occurring on the average of once in 10 years). For WWTPs without effluent diffusers, toxicity testing must be conducted on 100 percent effluent. With an effluent diffuser, the toxicity testing can be conducted at the instream waste concentration (IWC). Since the IWC of the existing WWTP is less than 1 percent, it would be advantageous not to have to conduct 100 percent effluent toxicity testing. The existing WWTP cannot pass the effluent toxicity test at 100 percent effluent.

State water quality standards also impact the future NPDES permit limits. Specifically, dissolved oxygen (DO) limits must be met at the WWTP's point of discharge. Also, since the production facility does not generate metal-bearing waste streams as defined in the OCPSF effluent

guidelines, water quality standards for metals will apply.

Regulatory Integration for Effective WWTP Improvements

Integration of RCRA and Clean Water Act compliance with the WWTP upgrade has presented numerous technical and logistical challenges.

Technical Challenges

The future WWTP will consist of preliminary treatment, biological treatment, clarification, effluent filtration, effluent diffusion into the river, and mechanical dewatering. The preliminary and biological treatment components are being driven by RCRA compliance. The clarifier modifications, effluent filtration, and effluent diffusion are being driven by Clean Water Act compliance. Mechanical dewatering is currently provided and will not be modified.

The future WWTP will be comprised entirely of above-ground tanks. These unit processes will meet the RCRA definition of a wastewater treatment unit and will therefore be exempt from permitting, design, and operational standards required for hazardous waste management units.

Recognizing that the future WWTP will handle characteristically hazardous wastewater, secondary containment will be provided for all of the new tanks. Although not required for compliance, this is being done to provide Responsible Care for wastes generated and managed on-site.

The influent pump stations will be designed to include secondary containment and leak detection. Above ground piping will be single-walled, and below ground piping will be double-walled.

The preliminary treatment system will be constructed over the former location of the settling basin and one of the equalization basins. The equalization tanks will also be equipped with leak detection. Each tank will be covered and vented to an air-pollution control system. Emergency power generation will provide backup power to major equipment in the event of a power failure.

The biological treatment system will be constructed over the former location of the second equalization basin and to the west of the aeration basins. The biological treatment system pump station will be designed to handle contaminated stormwater and process wastewaters segregated to by-pass preliminary treatment. Anaerobic treatment is being considered since it generates less sludge, allows control of volatile emissions, requires less energy, and generates biogas which can be recovered. However, its application on this wastewater is not proven, and pilot testing is underway to confirm performance. If anaerobic treatment is not feasible, tank-based aerobic treatment will be constructed.

A diversion tank will be constructed below grade to handle peak stormwater flow conditions and periods of

Table 2 - Clean Water Act Compliance Deadlines

Activity Description	Year/Quarter											
	1991				1992				1993			
	1	2	3	4	1	2	3	4	1	2	3	4
Regulatory Milestones:												
- OCPSF Statutory Compliance Deadline (March 31, 1989)												
- Submit Revised NPDES Permit Application				•	March 31, 1991							
- Comply with OCPSF Effluent Guidelines				•	September 30, 1991							
- Submit Stormwater NPDES Permit Application				•	November 18, 1991							
- Stormwater NPDES Permit Issued									•	November 18, 1992		
- Comply with Stormwater NPDES Permit (November 18, 1995)												
Construction:												
- Clarifier Modifications												
- Effluent Filter												
- Effluent Diffuser												

prolonged power failure. This tank will be constructed with both leak detection and secondary containment.

Logistical Challenges

The key logistical challenge in constructing the future WWTP is meeting the regulatory-driven schedule. There are two critical deadlines driving the construction schedule: (1) September 1991 for the new NPDES permit and (2) March 1993 for compliance with the LDR treatment standards for TC wastes. The WWTP modifications have been designated as either RCRA-driven or Clean Water Act-driven. Both are on critical path schedules for timely completion by the regulatory deadlines. Table 2 illustrates the implementation schedule for Clean Water Act-driven activities. Table 3 illustrates the implementation schedule for the RCRA-driven WWTP modifications.

The Clean Water Act-driven WWTP modifications are targeted for startup during the fourth quarter of 1991 to coincide with the new NPDES permit limitations. Since a compliance schedule was not negotiated, construction will have to be substantially complete, thereby requiring a fast-track approach to design and construction.

For the RCRA-driven modifications, an expanded implementation schedule is required to allow closure according to 40 CFR Parts 264/265 closure performance standards, multiple agency review, and closure certification. The RCRA-driven construction will take approximately two years to complete. The schedule is driven by the March 1993 deadline to replace the surface impoundments to comply with the LDR treatment standards for TC

wastes. Delays resulting from certifying closure of each basin could jeopardize the construction schedule and ultimately impact compliance with the March 1993 deadline to replace the surface impoundments.

The state environmental agency is responsible for construction permit approval. Process definition and predesign packages are being submitted to the agency for review prior to construction permit approval. Historically, this process has not been timely. Due to the complex phasing of this project, a program was established to conduct periodic meetings with the agency to expedite adjudication of review comments and obtain timely approvals.

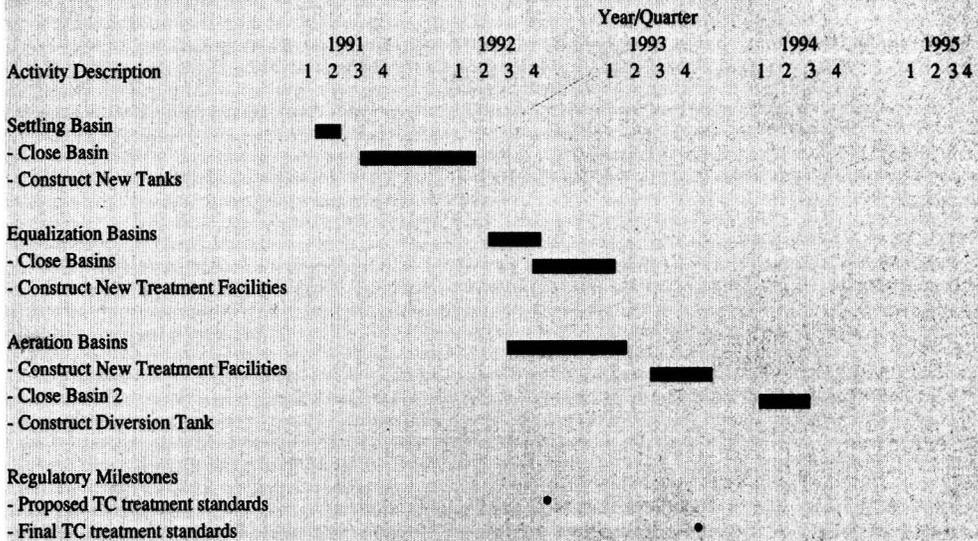
Construction sequencing is also critical from an implementation and cost standpoint. Production continuity must be maintained during the entire project. In addition, regulatory review and approval cycles have to be incorporated into the construction sequencing, making the contractor's construction period on-site longer and, thus, increasing costs.

Reaching Integration

The design and operating strategy for the future WWTP integrates foreseeable future RCRA and Clean Water Act compliance requirements. Unit processes for which the technical and regulatory design basis can be clearly defined will be incorporated into the project. For foreseeable future regulatory requirements that are not yet clearly defined but have a defined concept, flexibility will be incorporated into the design for later modifications.

Since the implementation schedule has two very tight

Table 3 - RCRA Regulatory Compliance Estimated Construction Schedule



regulatory-driven deadlines, a fast-track approach to design and construction is planned. The Clean Water Act-driven WWTP modifications will be complete in 1991, and the RCRA-driven modifications are scheduled for completion in 1994. However, regulatory approval cycles with multiple agencies, remediation and closure construction approaches, and RCRA design requirements (for example, secondary containment and leak detection) have significant impacts on the technical decisions and implementation schedules associated with the RCRA-driven

WWTP modifications. Therefore, implementation of all the WWTP modifications is on the critical path. To successfully implement this program, it will be necessary to integrate regulatory design requirements into the project early, coordinate existing production and WWTP operation to maintain continuity, conduct frequent and timely review meetings with the regulatory agencies, carefully manage uncertainties, and regularly prepare and update contingency plans.

Use of Risk Assessment Groundwater Model in Installation Restoration Program (IRP) Site Decisions

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Toxic chemicals have created much public concern over the past thirty years due to both environmental pollution and hazardous waste management. Hence, the associated Risk Assessment Process is both complicated and crucial in the outcome of decisions concerning remediation. Quantification for a particular contaminant can demonstrate that the concentration is adequately low, so that there is no need to carry out a remedial action, at that given site. The contaminant's specific calculated risk in a risk assessment is directly proportional to the average concentration of that contaminant chemical. The total risk is additive for all the contaminants present at that site, for both carcinogenic and non-carcinogenic risks. Further analysis into the risk assessment for a drum storage area at a DOD installation rendering airlift support for airborne forces resulted in elimination of an unnecessary and costly remedial action.

Introduction

Pollution from toxic chemicals and their waste generates concern because they affect human health, ecology, and non-living systems such as buildings, soil, water resources and air quality. Management of these hazardous chemicals and their disposal include both assessment of the risks of exposure and regulations to control these risks.

Quality data is necessary to assess the risk associated with toxic chemicals situated and disposed of at a site; quality data is also required to set priorities for clean-ups at such hazardous waste sites. This risk assessment process estimates total carcinogenic and noncarcinogenic risk at each site [1, 2, 3, 4, 5]. The total risk is the sum of the individual risk components associated with the intake of each toxic chemical along each exposure pathway, that is, inhalation, ingestion, and dermal contact. If the risk assessment outcome is borderline, then the individual risks may have to be further broken down for separate tar-

get organ systems within an overall living organism (mostly the human body). Thus, the risk assessment process can be very complicated and is very important, since decisions on remediations are based on the outcome.

The critical review of a contractor's risk assessment for a drum storage area at a military installation prevented a costly and unnecessary remedial action; taxpayer money was saved. This paper discusses the evaluation of that risk assessment. It shows how faulty mathematical calculations and questionable inclusion of a chemical as a compound of concern led to an apparent need for clean-up. When the risk was recalculated using valid data, correcting the faulty mathematical calculations and using appropriate chemicals of concern, no clean-up was required.

Background

The Installation Restoration Program (IRP) is a multi-disciplinary Department of Defense (DOD) program to assess and remediate hazardous waste problems on DOD

installations [7]. The IRP is driven by the requirements governing the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), the Superfund Amendments and Reauthorization Act of 1986 (SARA), and National Contingency Plan. The DOD uses the IRP to:

- Identify past hazardous materials/waste disposal and spill sites at active DOD/Air Force (AF) installations.
- Fully evaluate the environmental threat (if any) posed by these sites.
- Control migration of hazardous contaminants from the identified sites at each installation.
- Mediate hazards to public health, welfare, and the environment.
- Develop and evaluate necessary, feasible remedial actions for those hazardous sites.

These goals are realized thru a staged Remedial Investigation/Feasibility Study (RI/FS) process, in which conclusions and recommendations hinging on accurate and validated data, are used to structure and guide subsequent activities. The RI/FS process includes scoping to define data requirements and objectives, an RI to characterize sites for a baseline risk assessment, and an FS to define and evaluate alternative remedial actions from which a remedial action is selected. Thus, it is obvious that insuring the accuracy and usefulness of data collected is a critical step in the risk assessment, since the remedial action decision follows directly from the baseline risk assessment. The baseline risk assessment is the initial risk assessment at a given site where no remedial action has been taken.

The risk assessment for the drum storage area referenced above in the introduction to this paper involved three chemicals: (a) trans-1,2-dichloroethene (b) trichloroethylene (TCE); and (c) poly-chlorinated biphenyls (PCBs) (1260 arochlor). However, the concentration of the trans-1,2-dichloroethene (noncarcinogenic compound) was negligible for all environmental sectors (surface water with surrounding sediments, groundwater, surface and subsurface soils, and air) so that in this risk assessment only the TCE and PCBs were considered. For TCE and PCBs, the primary risks are carcinogenic; non-carcinogenic risks were not pertinent for this case and only the chronic intake doses are relevant. The primary errors in the original baseline risk assessment were that:

- The average TCE concentration was based on only part of the data set resulting in a concentration value almost double the actual average over all data points.
- A major part of the risk value resulted from the PCB-1260, which was based on an average PCB-1260 concentration over 3 monitoring wells consisting of 2 non-detect values and one estimated value below the method detection limit.

Other considerations in the risk assessment include:

- The use of nearby bodies of water for example, are

they drinking water supplies or not.

- The surface water analytical results.
- The rate of migration for the distance between the contaminant source and the point of exposure.

Analytical Models/Methodology

Initially, overall chronic intake dosages of the TCE and PCBs were estimated. These intake dosages were then multiplied by the slope factors (also known as carcinogenic potency factors) to compute the risk component from that given chemical for that specific exposure pathway. The risk assessment is completed when the individual risk components are summed into the total site risk value. The three potential exposure pathways involved in this risk assessment were:

- ingestion of water via drinking.
- inhalation from showering.
- dermal exposure from bathing.

The concentrations of these chemicals were found to be negligible in the air, surface water, and both surface and subsurface soils. Consequently, inhalation exposure results only from inhaling volatiles during showering in contaminated groundwater, since levels are negligible in the surface water and air, and ingestion exposure results only from drinking this groundwater. There would be no ingestion nor dermal exposure for very young children eating or contacting surrounding soils because soils are uncontaminated and access to the site is restricted. Swimmers ingesting or contacting surface water would not be exposed because surface water is uncontaminated. The only possible dermal contact would result from bathing in contaminated groundwater. It is worth noting that there are presently no wells drawing water from the zone of groundwater contamination (the contaminated plume). Therefore, the calculated ingestion exposure due to drinking the contaminated groundwater is an overestimate of actual exposure due to drinking. The ingestion term is calculated as if it were an active drinking water source to err on the side of caution, therefore demonstrating conservatism in the risk assessment.

It is worth noting that the chronic intake dosages in the risk assessment process are further considerably overstated since these do not take into account the body's metabolism and elimination of chemicals. If a comprehensive material balance on a chemical in the body were carried out, accumulation, generation/ metabolism, intake, and elimination (outflow) would be considered. Thus, the net chronic intake dosage would be expressed in the accumulation term as the difference between intake and elimination. The generation term in a material balance would further reduce overall chronic dosage, since the body does not produce the specific chemical, but metabolizes it to some degree. Thus, the overstated chronic intake dosages result in a higher final assessment of the risk - this is more conservative, in that it errs for caution.

Calculation of Exposure from Ingestion

$$\text{Intake} \left(\frac{\text{mg}}{\text{kg} - \text{day}} \right) = \frac{(CW)(IR)(EF)(ED)}{(BW)(AT)} \quad (1)$$

For a conservative upper bound estimate on the intake, it is assumed that $EF \cdot ED / AT = 1$, that is, $EF = 365$ days/yr, $ED = 70$ years, and $AT = 70 \cdot 365$ days = 25,550 days. Studies have shown that on the average 75% of water consumption is for home use [8]. At this site, actual exposure is far less, since this site is strictly a work area with no residential area nearby. Thus, Eq. (1) simplifies to Eq. (2).

$$\text{Intake} \left(\frac{\text{mg}}{\text{kg} - \text{day}} \right) = \frac{0.75(CW)(IR)}{(BW)} \quad (2)$$

The IR value is taken as 2 liters/day [1, 5]. The BW is the average adult body weight of 70 kg [1, 5].

Calculation of Exposure from Inhalation

$$\text{Intake} \left(\frac{\text{mg}}{\text{kg} - \text{day}} \right) = \frac{(CA)(IR)(ET)(EF)(ED)}{(BW)(AT)} \quad (3)$$

Similar to ingestion, $EF \cdot ED / AT = 1$, that is, $EF = 365$ days/yr, $ED = 70$ years, and $AT = 70 \cdot 365$ days = 25,550 days.

$$\text{Intake} \left(\frac{\text{mg}}{\text{kg} - \text{day}} \right) = \frac{(CW)(IR)(VW_{sh})}{(BW)} \left(\frac{SD}{SV} + \frac{BD}{BV} \right) \quad (4)$$

Note that $CW \cdot VW_{sh} / SV$ and $CW \cdot VW_{sh} / BV$ represent CA for the shower process and additional bathroom exposure after showering, respectively. Furthermore, for shower $ET = SD$ and $ET = BD$ for additional bathroom exposure time after showering. Thus, Eq. (3) becomes Eq. (4). The IR value is taken as the average adult value of 20 m³/day, see pp. 6-44 in Risk Assessment Guidance for Superfund - Vol. I - Human Health Evaluation Manual [1]. The BW is the average adult body weight of 70 kg [1, 5]. The other values pertinent to Eq. (3) and (4) include: $SD = BD = 10$ minutes (1/6 hours); and $SV = 3$ m³; and $BV = 10$ m³ [8]. In addition, a conservative approach for calculating inhalation dosage assumes that TCE volatilizes completely. However, PCB does not volatilize, therefore PCB would not contribute to any chronic inhalation exposure.

Calculation of Exposure from Dermal Contact

$$\text{Intake} \left(\frac{(CW)(SA)(PC)(ET)(EF)(ED)(CF)}{(BW)(AT)} \right) \quad (5)$$

Similar to ingestion and inhalation, $EF \cdot ED / AT = 1$, that is, $EF = 365$ days/yr, $ED = 70$ years, and $AT = 70 \cdot 365$ days = 25,550 days. Thus, Eq. (5) simplifies to Eq. (6).

$$\text{Intake} \left(\frac{\text{mg}}{\text{kg} - \text{day}} \right) = \frac{(CE)(SA)(MF)(ET)(CF)}{(BW)} \quad (6)$$

The SA value is taken as the average adult value of 18,150 cm² [1, 5], and BW as the average adult body weight of 70 kg [1, 5]. The MF is taken as 0.5 mg/cm²-hr, since this was found to be 0.4336 mg/cm²-hr in an absorption study [9]. This corresponds to a PC value of 5.0×10^{-4} cm/hr, since the TCE is at sufficiently low concentrations such that it can be deemed as a dilute aqueous medium. As will be illustrated in the Results, the risk associated with dermal contact is very small compared with that from ingestion and inhalation, such that if a PC value of 8.4×10^{-4} cm/hr [1] were used, the risks from dermal exposure would still be more than 2 orders of magnitude less than the specific risks from the ingestion and inhalation exposure pathways.

For all of the exposure pathways, the contractor applied a factor of 58/68 to the chronic intakes to give a weighted chronic intake for adults, where 58 is the number of years as an adult out of a 68-year lifetime. Due to large uncertainty in expected exposures for the 0-2 age category in most cases, the lifetime adjustment takes away these two years and the factor applied is 58/68 instead of 58/70, in order "to lean on the conservative side of the doubt". The pre-teenage (less than 12) group could not possibly be present at this site. In addition, assuming that the adult period starts at age 12 is extremely strict, since a work zone would not likely have anyone present under the age of 18, and certainly not under the age of 16. Perhaps, inherent in this assumption, is that the 12-18 group may be present in sporadic amounts by visits, so this age group is counted as if they were present on a regular basis. Therefore, a factor of 52/68 or 54/68 would have been more reasonable, but to err on the side of caution, the stricter factor of 58/68 was retained in this review of the contractor's risk assessment.

Route/Chemical Specific Risk

$$R_{ij} = (SF_{ij}) \cdot (\text{Intake})_{ij} \quad (7)$$

dimensionless $\frac{\text{Kg} - \text{day}}{\text{mg}} \cdot \frac{\text{mg}}{\text{Kg} - \text{day}}$

Note that risk values are dimensionless, since slope factors have units reciprocal to those of intake. Risk numbers denote frequency of excess cancer cases above what is to be expected for environmental backgrounds (250,000 cases per million people, about a quarter, due to natural environmental factors). If the risk is 2×10^{-4} , then there would be 2 excess cancer cases in 10,000 people over those expected

under environmental background levels [1]. The slope factors (SFs) were obtained from the EPA IRIS (Integrated Risk Information System). For TCE, the most recent SF is from 7/1/89, and for PCBs, the most recent SF is from 5/1/89.

These SFs can be obtained from six sources with the following priority (see pp. 7-13 - 7-15 from [1]).

- (i) IRIS.
- (ii) HEAST - Health Effects Assessment Summary Tables, which are updated quarterly.
- (iii) EPA Criteria Documents.
- (iv) Agency for Toxic Substances and Disease Registry (ATSDR) toxicological profiles.
- (v) EPA's Environmental Criteria and Assessment Office.
- (vi) Open literature.

Total Risk

Total Risk = R = Sum of all Risks from Eq.(7) (8)

$$R = \sum_{i=1}^3 \sum_{j=1}^2 R_{ij} = \sum_{i=1}^3 \sum_{j=1}^2 (SF_{ij})(Intake)_{ij} \quad (9)$$

Note that total risk is obtained by summing over both chemicals and over the three exposure pathways. Since PCB is not volatilized at all, only 5 chemical/exposure pathway specific risks are added into the total risk calculation: ingestion of PCB and TCE; dermal contact of PCB and TCE; and inhalation of TCE.

Results

The first step in analyzing the risk for any given exposure pathway is to determine average concentrations of the specific analytes in that medium, applicable to the exposure pathway. The three above noted exposure pathways indicate that the only environmental medium of concern is the groundwater. Therefore, the average concentrations of the TCE and PCB must be determined. For these two chemicals, the results of measurement are normally reported in ug/l. However, these are shown in mg/l in order to obtain the chronic intakes in (mg/kg-day) since the slope factors are in reciprocal (mg/kg-day) and the risk is dimensionless.

For the TCE, there were a total of 6 measurements from 4 monitoring wells (MWs):

- MW-1: 0.0027 mg/l
- MW-2: 0.0081 mg/l
- MW-3: 0.08, 0.016, and 0.17 mg/l
- MW-4: 0.026 mg/l

The average of these 6 readings is 0.05 mg/l, but it is unclear as to which numbers should be entered into this average, since 3 of these readings came from MW-3 and these 6 readings were not all taken at the same time. Therefore, the average of the 4 wells was taken, where only

the highest reading from MW-3 was retained. This average is 0.0517 mg/l, which is slightly above the 0.05 mg/l value. Moreover, if a weighed average at MW-3 were taken, and this were averaged with the other 3 wells, then the average would be even lower at 0.0314 mg/l. Hence, the 0.05 mg/l average TCE concentration serves as a solid conservative upper bound estimate. However, in this risk assessment, the contractor used an average concentration of 0.0895 mg/l, which seemed to average the MW-2 and highest MW-3 readings, and ignored the other 4 measurements. This resulted in an almost double value for the TCE risks. All TCE-readings were well above the method detection limit of 0.0006 mg/l [7].

For the PCB, there were a total of 3 measurements from 3 monitoring wells (MWs):

- MW-1: 0.00081 mg/l (estimated)
- MW-2: none detected
- MW-3: none detected

For the "none detected" measurements, 0.0005 mg/l, half the value of the 0.001 mg/l [7] method detection limit, is entered into the average to assure that a conservative estimate is taken. Thus, the average concentration for PCB is 0.0006 mg/l, considerably below the detection limit. Consequently, the PCB-risk is negligible, since the concentrations are below the method detection limit. Thus, it is highly questionable whether the PCB should have been deemed a chemical of concern at this site. However, the PCB-risk component is added here to show an upper bound risk for these site conditions.

A comparison of the risk assessment performed for average TCE concentrations of 0.05 mg/l and 0.0895 mg/l follows as shown in Tables 1 and 2. The intakes are computed using Eq. (2), (4), or (6), depending on the exposure pathway calculated. The factor of 58/68 is then applied to the intake to give the weighted intake, which in turn is multiplied by the slope factor (SF) to give the specific risks for the particular exposure pathway and given chemical. The sum of all of the specific risks then gives the total risk for the site, which in this case is a carcinogenic risk.

From Figure 1, it is evident that the quality of the risk assessment can make a crucial difference in the outcome in a remedial action decision. In case "a", where the PCB-risk component was discarded and the correct average TCE-concentration at 0.05 mg/l was used, the total risk is 6×10^{-5} , well below the EPA threshold for acceptable cancer risk. In case "b", the total risk is 1×10^{-4} , when the PCB-risk component was discarded and the erroneous higher average TCE-concentration at 0.0895 mg/l was used. In case "c", where the PCB-risk component was included and the correct average TCE-concentration at 0.05 mg/l was used, the total risk is 1×10^{-4} . In case "d", the total risk is 2×10^{-4} , when the PCB-risk component was included and the erroneous higher average TCE-concentration at 0.0895 mg/l was used.

TABLE 1 - Risk Assessment (TCE Concentration = 0.05 mg/l)

Chemical	CW (mg/l)	Pathway/Equation	Intake (mg/kg-day)
TCE	0.05	Ingestion/(2)	1.071×10^{-3}
PCB-1260	0.0006	Ingestion/(2)	1.286×10^{-5}
TCE	0.05	Inhalation/(4)	4.299×10^{-3}
PCB-1260	0.0006	Inhalation/(4)	non-volatile
TCE	0.05	Dermal Contact/(6)	1.080×10^{-6}
PCB-1260	0.0006	Dermal Contact/(6)	1.296×10^{-8}

Weighted intake (mg/kg-day)	SF (mg/kg-day) ⁻¹	Specific Risk
9.139×10^{-4}	0.011 (ingest)	1.005×10^{-5}
1.097×10^{-5}	7.7 (ingest)	8.444×10^{-5}
3.667×10^{-3}	0.013 (inhale)	4.767×10^{-5}
non-volatile	7.7 (inhale)	non-volatile
9.215×10^{-7}	0.011 (dermal)	1.014×10^{-8}
1.106×10^{-8}	7.7 (dermal)	8.514×10^{-8}

The total risk sum of the specific risks is approximately 1.4×10^{-4} , which, rounding to one significant figure in accordance with USEPA instructions, gives a risk of 1×10^{-4} . This is within the acceptable range for USEPA (1, 4, 5).

TABLE 2 - Risk Assessment (TCE Concentration = 0.0895 mg/l)

Chemical	CW (mg/l)	Pathway/Equation	Intake (mg/kg-day)
TCE	0.0895	Ingestion/(2)	1.918×10^{-3}
PCB-1260	0.0006	Ingestion/(2)	1.286×10^{-5}
TCE	0.0895	Inhalation/(4)	7.695×10^{-3}
PCB-1260	0.0006	Inhalation/(4)	non-volatile
TCE	0.0895	Dermal Contact/(6)	1.934×10^{-6}
PCB-1260	0.0006	Dermal Contact/(6)	1.296×10^{-8}

Weighted intake (mg/kg-day)	SF (mg/kg-day) ⁻¹	Specific Risk
1.636×10^{-3}	0.011 (ingest)	1.799×10^{-5}
1.097×10^{-5}	7.7 (ingest)	8.444×10^{-5}
6.563×10^{-3}	0.013 (inhale)	8.533×10^{-5}
non-volatile	7.7 (inhale)	non-volatile
1.649×10^{-6}	0.011 (dermal)	1.814×10^{-8}
1.106×10^{-8}	7.7 (dermal)	8.514×10^{-8}

The total risk sum of the specific risks is approximately 1.9×10^{-4} , which, rounding, gives a risk of 2×10^{-4} . This falls in the high risk category according to USEPA guidelines (1, 4, 5). Note the difference in the specific risks for the TCE exposures, for all three exposure pathways.

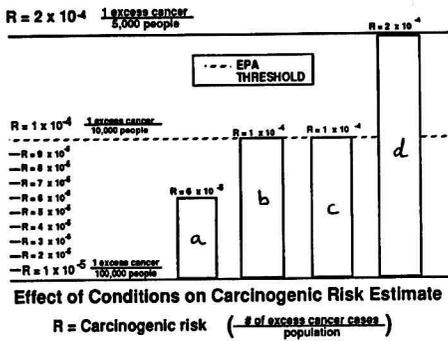


Figure 1. Effect of conditions on carcinogenic risk estimate. a) PCB-risk component discarded and correct average TCE-concentration at 0.05 mg/l; b) PCB-risk component discarded and erroneous higher average TCE-concentration at 0.0895 mg/l; c) PCB-risk component included and correct average TCE-concentration at 0.05 mg/l; d) PCB-risk component included and erroneous higher average TCE-concentration at 0.0895 mg/l.

Conclusion

The calculated risk reduction which resulted from using the corrected average TCE concentration allowed the Air Force to place this site in the No Further Action (NFA) status. Moreover, since the PCB concentrations for all data points were below the method detection limit, while a major part of the calculated risk value was due to the PCB component in the ingestion of drinking the groundwater supplies, further questions arose concerning the wisdom pursuing a costly remedial action at this site. The Air Force was considering an expensive pump and treat remedial action, which would have been of little value at this site.

Other factors considered in arriving at the NFA decision include the absence of both TCE and PCB in all of the other environmental media, namely air, soils, and near-by surface water and sediments. Furthermore, the groundwater present at the site is not used as an active drinking water source, since the drinking water is provided to all users both on and near this installation by the local township from an alternate water source. In addition, the closest municipal well drawing from the alternate water source is approximately three miles upstream from this installation. Since there was no PCB nor TCE detected in the alternate water source nor in surface water, no contamination problem of domestic groundwater supplies is apparent. In addition, although surface water receives discharge from the contaminated groundwater, no contaminants were

identified in the surface water.

In summary, when performing a risk assessment, particular attention must be paid to the media of the pathways analyzed, methods of analysis, fate and transport of the environmental contaminants, as well as proper quality assurance and quality control of data and mathematical operations to insure a valid portrayal of risk. Figure 2 illustrates data quality from the perspective of the macroscopic view of numerous engineering firms.

Acknowledgements

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Notation

- AT = time interval over which the exposure is averaged, days
- BD = average additional exposure time in bathroom after shower, hours
- BV = volume of bathroom, m³
- BW = body weight (70 kg for average adult)
- CA = concentration of chemical in air, mg/m³
- CF = conversion factor (1 liter/1000 cm³ or 1 liter/106 mg)
- CW = concentration of chemical in water, mg/l
- ED = exposure duration, years
- EF = exposure frequency, days/year
- ET = exposure time, hours/day
- Intake = dose intake over the lifetime interval, mg/(kg-day)
- IR = intake rate (2 l/day in drinking water; 20 m³/day in breathing air)
- MF = mass flux, mg/hr-cm²

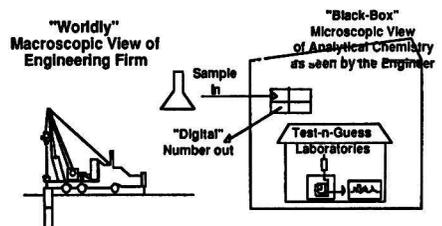


FIGURE 2. Quality in perspective.

PC = chemical-specific dermal permeability constant, cm/hr
 PCB = polychlorinated biphenyl
 R = total risk
 R_{ij} = the exposure route/chemical specific risk
 SA = skin surface area of exposure, cm²
 SD = duration of shower, hours
 SV = volume of the shower stall, m³
 SF = slope factor (carcinogenic potency factor), kg-day/mg. SFs are obtained from EPA's IRIS(Integrated Risk Information System)
 SF_{ij} = slope factor for exposure pathway i and chemical j
 TCE = trichloroethylene
 VW_{sh} = average amount of water used during a shower (100 liters)

Subscripts

i = 1, 2, and 3 for the exposure pathways (ingestion of drinking water, inhalation during a shower, and dermal contact from taking a bath, respectively)
 j = 1, and 2 for the chemicals (TCE, and PCB, respectively)
 sh = during the shower process

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Kinetics of Sulfur Dioxide Uptake on Supported Cerium Oxide Sorbents

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A thermogravimetric technique has been used to evaluate the apparent rate of SO₂ absorption by ceria supported on alumina. A kinetic model for the sulfation of the CeO₂/Al₂O₃ sorbent has been developed that is first order with respect to the partial pressure of SO₂ and first order with respect to the fractional unreacted cerium oxide on the sorbent. The reaction was also found to be zero order with respect to the oxygen and water vapor content of the gas over a range of concentrations that might reasonably be encountered in actual flue gas streams. CeO₂/Al₂O₃ sorbent is being studied at the Pittsburgh Energy Technology Center as a potential new sorbent for simultaneous removal of 90+% of both SO₂ and NO_x from coal combustion flue gas in a dry, regenerable process.

Introduction

Several promising new methods are being developed at the Pittsburgh Energy Technology Center (PETC) to remove the sulfur and nitrogen oxides from the flue gas of coal-fired utility boilers. The Fluidized-Bed Copper Oxide Process developed at PETC is one such new technology for the simultaneous removal of 90% of both SO₂ and NO_x from the flue gas [1-3]. This process involves the absorption of SO₂ by copper oxide on an alumina support in conjunction with sorbent catalyzed reduction of NO_x by ammonia addition. Alternate sorbents to CuO/Al₂O₃ are also being considered at PETC for possible improvements in reactivity toward SO₂, regenerability, attrition resistance,

and sorbent costs. A similar process concept based on a CeO₂/Al₂O₃ sorbent [4, 5] is being studied in our laboratory and is the subject of this report.

Cerium oxide is a particularly promising new sorbent: ceria improves resistance of alumina to thermal loss of surface area [6]; CeO₂ sorbent reacts with SO₂ over a fairly wide temperature range; and when regenerated under the appropriate conditions, CeO₂/Al₂O₃ sorbent produces an off-gas stream that can be used conveniently in a Claus plant for conversion into elemental sulfur [4]. The natural abundance of cerium is slightly greater than that of copper, and extensive deposits are located in the western United States as well as in Australia, Brazil, India, and China. Rare earth minerals are mined both as a primary product

and as a by-product of the mining of such metals as iron (in China), tin, titanium, and zirconium. Cerium is produced as a by-product of the isolation of other rare earths, and is currently readily available at moderate prices [7]. It should be pointed out, however, that the expensive step in supported sorbent preparation is fabrication of the alumina spheres.

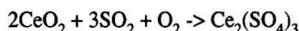
Experimental

Sorbent samples were prepared by aqueous impregnation of 1.6 mm (1/16 in.) diameter alumina spheres. Reagent-grade, water-soluble cerium salts that can be decomposed thermally at moderate temperatures were used, and the alumina spheres were obtained from commercial catalyst manufacturers. The effects of sorbent preparation on the reactivity of $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents toward SO_2 and on the regenerability of the sorbents have been previously described, along with details of the thermogravimetric (TG) technique used in our laboratory [8].

Simulated flue gas was blended from certified gas mixtures and humidified by sparging through water at constant temperature. The calculated typical gas composition was 2,800-3,000 ppm SO_2 ; 480-500 ppm NO ; 2.8-3.0 % O_2 ; 13.7-14.7 % CO_2 ; 4.0, 7.0, or 18 vol % H_2O ; and N_2 as the balance; other gas compositions are described below. The dry gas flow rate through the 25 mm ID reactor was $3.05 \times 10^{-6} \text{ m}^3/\text{s}$ (STP), which was sufficient to maintain differential reaction conditions with respect to SO_2 for the most reactive sorbents. A sample size of 50 mg of sorbent was selected to just fill the quartz sample pan; this corresponds to about 18-20 of the spherical pellets. A typical TG test sequence was composed of four steps: 1) the sample was heated to the desired reaction temperature at $10^\circ\text{C}/\text{min}$ in dry N_2 ; 2) after allowing the sample to come to equilibrium at the test relative humidity, a "dry" sample weight was obtained and then the sample was exposed to humidified simulated flue gas for one hour; 3) the sample was regenerated by reduction in H_2 for 30 min followed by reoxidation in air for 10 min; and 4) the sample was re-exposed to flue gas for 60 min.

Since cerium nitrates are thermally unstable above 250°C and hydrated ceric sulfate is completely dehydrated at approximately 350°C [9], all of the weight gain observed during the TG tests, which were conducted above 350°C , has been attributed to sulfate formation. X-ray diffraction results for several of the spent $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbent samples showed weak lines not present in the fresh sorbent. However, these lines could not be assigned to known cerium sulfate compounds and suggested that the CeO_2 is converted to an amorphous or highly dispersed sulfate on exposure to flue gas. Examination of fresh and spent sorbent by FTIR (Fourier transform infrared spectroscopy) clearly showed the presence of sulfate on the spent sorbents, but specific product compounds could not be identified. Fresh, regenerated, and spent sorbents were

also examined by XPS (X-ray photoelectron spectroscopy). The fresh and regenerated sorbents were found to contain CeO_2 and the regenerated sorbent also contained small amounts of sulfate, but no detectable sulfide. The fully sulfated sorbent was found to contain predominantly Ce(III) . (The presence of small amounts of Ce(IV) cannot be ruled out from the cerium photoelectron spectra.) The weight gain observed during the TG tests was therefore analyzed using the following equation:



Results And Discussion

Reactivity measurements for $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents have been made in the thermogravimetric analyzer (TGA) test unit to examine the kinetics of SO_2 sorption as a function of gas composition, sorbent metal loading, and experimental conditions.

First, the data collected in the TGA test unit were evaluated for suitability for kinetic determinations. Gas phase diffusion limitations on the rate of SO_2 sorption measured in this unit were examined. Tests were conducted to verify that bulk gas phase mass transfer was not limiting the measured SO_2 uptake: first, the total gas flow rate was doubled, and then a larger, more open sample basket was substituted to contain the sorbent. Results in both these tests were equal to rates determined previously with lower flow rate and a shallow, closed-bottom basket; therefore, any diffusional limitation that occurs is characteristic of the reacting system and is not an artifact of the experimental equipment. The reactor vessel was also partially filled with fused silica pellets to substantially reduce the void volume and the results were compared to earlier runs. It was determined that the true reaction starting time could satisfactorily be estimated by simply subtracting the "dead" time required to fill the vessel to the level of the sample basket.

The effect of flue gas composition on the rate of SO_2 sorption by $\text{CeO}_2/\text{Al}_2\text{O}_3$ was examined in detail at 600°C . The rate of SO_2 uptake was found to be independent of the relative humidity over the range 4 to 18 vol % H_2O , independent of the CO_2 concentration over the range 0% to 15%, independent of the NO concentration over the range 0 to 500 ppm, and, somewhat surprisingly, independent of the O_2 concentration over the range 2.8% to 12.7%.

Reaction Order with Respect to Sulfur Dioxide Concentration

The reaction order with respect to SO_2 concentration was determined using the differential method, that is, by measuring the initial slopes of the TG curves. A rate law of the following form was assumed:

$$r = da_c/dt = kP_s^n a_c^m \quad (1)$$

REACTION ORDER FOR SO₂

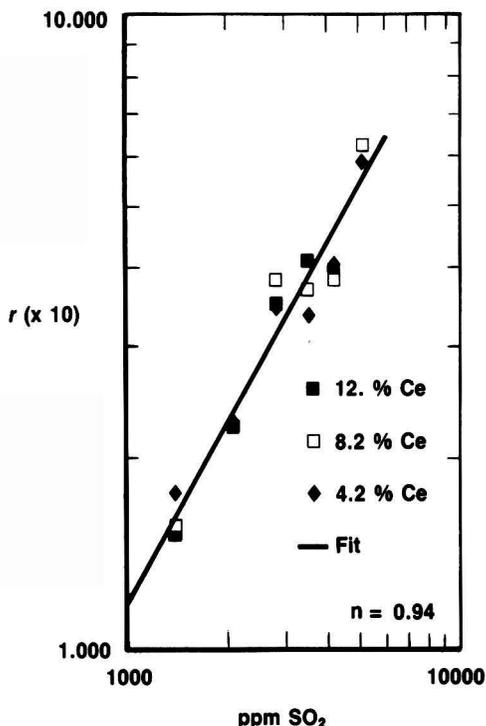


FIGURE 1. Double-logarithmic plot of initial rate of SO₂ uptake, r , by CeO₂/Al₂O₃ sorbents against partial pressure of SO₂, P_s .

where a_c is the cerium loading on the sorbent, and P_s is the partial pressure of SO₂ in the flue gas. As pointed out above, the TGA test unit was operated as a differential reactor with respect to SO₂, i.e., the concentration of SO₂ remained constant throughout an individual test run. (Although the SO₂ concentration was not measured during these tests, at typical test conditions the rate of addition of SO₂ to the reactor was approximately 2.4 mmole/min., and the typical 50 mg sample of 12% Ce sorbent contained only 0.044 mmole CeO₂. Complete reaction of the sorbent within the first minute could have consumed less than 3% of the total SO₂ flowing into the reactor). For short reaction times, the concentration of CeO₂ remaining on the sorbent pellet will not differ appreciably from the starting concentration and the rate law may be written:

$$r = \text{const. } P_s^n \quad (2)$$

Taking the logarithm of both sides of this equation yields,

$$\log r = \log \text{const.} + n \log P_s \quad (3)$$

The reaction order, n , can be determined from a double-logarithmic plot of rate against SO₂ concentration. Figure 1 shows this double-logarithmic plot for the initial slope of the TG curves, for sorbents of three different metal loadings. The SO₂ concentrations ranged from 1400 ppm to 5100 ppm. The slope of the least squares straight line through this data is 0.94, indicating that the reaction is first order with respect to SO₂ concentration.

Reaction Order with Respect to Consumption of the Sorbent

In general, the integrated rate law for a first order reaction can be written as

$$kt = \ln[a/(a-x)] \quad (4)$$

where a is the initial concentration of the reactant and x is the concentration that has been consumed at time t . By considering the data for a single test, the reaction order with respect to time can be determined for the sorbent. Figure 2 shows a plot of Equation 4 for a typical TG test. Although a straight line does not fit the data throughout the entire consumption of the sorbent, the curve is linear up to approximately 75 to 80 percent con-

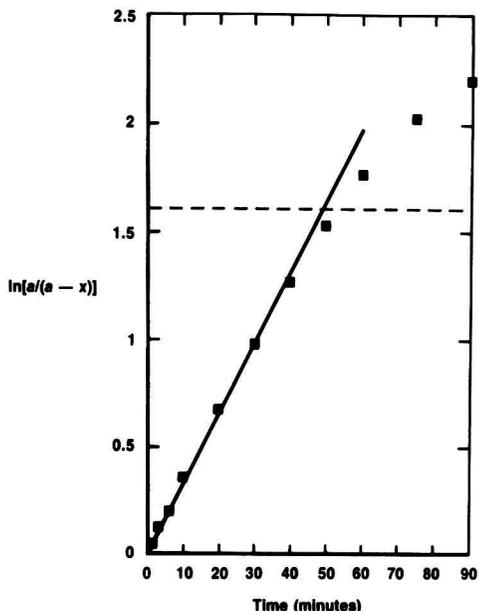


FIGURE 2. Test for first-order kinetics of the consumption of CeO₂ for a typical TG test (2800 ppm SO₂, 600°C, 12% Ce sorbent.) Dashed line represents 80 percent conversion of the CeO₂. Solid line represents linear least squares fit for data from the first 30 min.

version of the CeO_2 on the sorbent. (The dashed line in Figure 2 represents 80 percent conversion). The reaction can, therefore, be adequately described as first order with respect to consumption of the sorbent except as the sorbent nears complete saturation. Diffusional effects probably contribute significantly at very high sorbent utilization; however, this high sorbent utilization region is not normally approached under practical process operations.

The rate of consumption of the sorbent can therefore be written as

$$da_c/dt = kP_s a_c \quad (5)$$

Determination of the rate constant

The rate constant k can be determined from the integrated form of the equation

$$kP_s t = \ln[a_c/(a_c - x_c)] \quad (6)$$

(Recall that in the TGA test unit, the concentration of SO_2 is constant.) Figure 3 summarizes data for a large number of TG tests conducted at 600°C using 2,800 ppm SO_2 in the simulated flue gas. Each point represents an average value for 4 to 10 replicate determinations. Data is included for each of the three metal loadings for CeO_2 conversions up to approximately 50 percent. Clearly, the slopes of the lines represented by the data for the three metal loadings, and therefore the rate constants for Equation 6, are different. A single rate constant that represents all the data for all

CONSUMPTION OF CeO_2 SORBENT

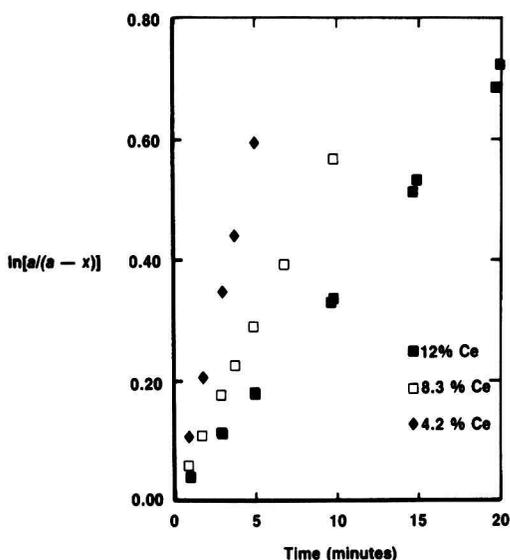


FIGURE 3. Determination of first-order rate constant k using Equation 6 for three different sorbent metal loadings.

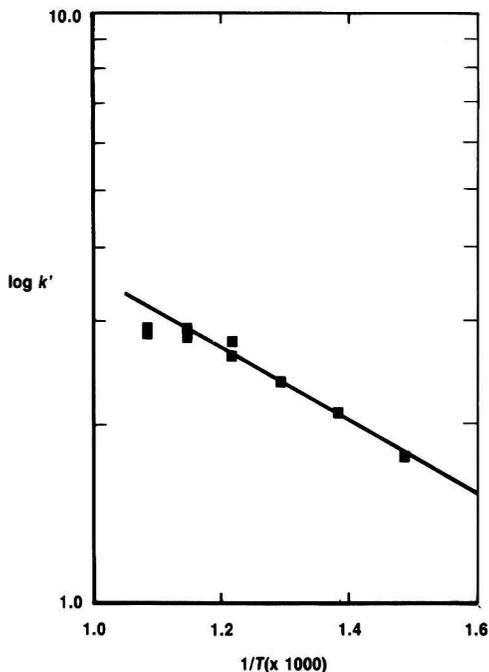


FIGURE 4. Arrhenius law plot for SO_2 uptake by $\text{CeO}_2/\text{Al}_2\text{O}_3$ sorbents over the temperature range 673 to 923 kelvin. Linear least squares fit line is for data over the range 673 to 873 kelvin only.

three metal loadings may be obtained by multiplying the rate constant of Equation 6 times the metal loading on the individual sorbent,

$$k' = ka_c = a_c \{ \ln[a_c/(a_c - x_c)] \} / P_s t \quad (7)$$

Table 1 compares the calculated rate constants from Equations 6 and 7 for the data sets plotted in Figure 3. The average value of k' for the values reported in Table 1 (data taken at 600°C) is 0.028 ± 0.002 [%Ce $\text{s}^{-1}\text{kPa}^{-1}$]. Careful examination of the calculated rate constants, in Table 1 shows some slight drift in the values. However, a simple first order rate equation describes the conversion of the sorbent reasonably well.

Temperature Dependence of the Rate Constant

Sorbent reactivity data from the TG tests was also analyzed using Equation 7 for temperatures ranging from 650°C to 400°C . The temperature dependence of the rate constant k can be described by the Arrhenius law,

$$k = A \exp(-E/RT) \quad (8)$$

where A is a constant which is usually known as the fre-

**Table 1 - Comparison of Rate Constant Calculated from Equations 6 and 7.
Data are for 600°C and 2,800ppm SO₂**

Cerium Loading (%)	x _c (%)	Time (seconds)	k (s ⁻¹ kPa ⁻¹)	k' (%Ce s ⁻¹ kPa ⁻¹)
12.1	0.467	57	2.5x10 ⁻³	3.0x10 ⁻²
	1.279	177	2.3x10 ⁻³	2.7x10 ⁻²
	1.984	297	2.2x10 ⁻³	2.6x10 ⁻²
	3.396	575	2.1x10 ⁻³	2.5x10 ⁻²
	4.857	874	2.1x10 ⁻³	2.5x10 ⁻²
	5.992	1,174	2.1x10 ⁻³	2.5x10 ⁻²
12.2	0.470	59	2.4x10 ⁻³	2.9x10 ⁻²
	1.280	179	2.2x10 ⁻³	2.7x10 ⁻²
	1.987	299	2.1x10 ⁻³	2.6x10 ⁻²
	3.477	584	2.1x10 ⁻³	2.5x10 ⁻²
	5.048	889	2.2x10 ⁻³	2.6x10 ⁻²
	6.282	1,189	2.2x10 ⁻³	2.7x10 ⁻²
8.2	0.469	52	4.0x10 ⁻³	3.3x10 ⁻²
	0.849	103	3.8x10 ⁻³	3.1x10 ⁻²
	1.327	172	3.7x10 ⁻³	3.0x10 ⁻²
	1.653	223	3.6x10 ⁻³	3.0x10 ⁻²
	2.066	292	3.6x10 ⁻³	3.0x10 ⁻²
	2.671	403	3.5x10 ⁻³	2.9x10 ⁻²
	3.557	583	3.5x10 ⁻³	2.9x10 ⁻²
	4.427	54	7.2x10 ⁻³	3.0x10 ⁻²
4.2	0.772	103	7.1x10 ⁻³	3.0x10 ⁻²
	1.222	174	7.2x10 ⁻³	3.0x10 ⁻²
	1.485	223	7.1x10 ⁻³	3.0x10 ⁻²
	1.866	294	7.2x10 ⁻³	3.0x10 ⁻²

quency factor, E is the activation energy, R is the gas constant, and T is the absolute temperature. Equation 8 may also be written.

$$\ln k = -E/RT + \ln A \quad (9)$$

The Arrhenius law was tested for the TG data for the CeO₂/Al₂O₃ sorbent-SO₂ reaction by plotting the logarithm of k' (calculated using Equation 7) against the reciprocal of the absolute temperature. Results are shown in Figure 4. Examination of the data presented in Figure 4 shows that the apparent rate constant begins to level off above approximately 600°C. This is consistent with the onset temperatures for sulfate decomposition reported in the literature for several cerium sulfate compounds [9,10] and may indicate the thermal onset of reversibility of the reaction. Another possible explanation for the decrease in apparent rate is a high temperature pore diffusion effect, the transition from a region of intrinsic surface reaction control of the rate to a region of significant pore diffusion, the internal-diffusion regime [11]. The work presented here does not address the relative contributions of these two effects; however, the cerium oxide process is not expected to be operated beyond 600°C in future PETC studies. The least squares straight line fit to the data over the temperature range 600°C to

400°C yields an activation energy E = 12 [kJ/mole] and a frequency factor A = 0.14 (%Ce s⁻¹kPa⁻¹).

Conclusion

The absorption of SO₂ on CeO₂/Al₂O₃ sorbents has been found to follow a simple kinetic model which is first order with respect to the partial pressure of SO₂ and approximately first order with respect to the fractional unreacted CeO₂ on the sorbent. An empirical rate equation was developed

$$k'P_s t = a_c \ln[a_c/(a_c - x_c)]$$

$$k' = 0.028 \pm 0.002 \text{ (% Ce s}^{-1}\text{kPa}^{-1} \text{ at } 600^\circ\text{C)}$$

The temperature dependence of the rate of reaction can be described by an Arrhenius law dependence of the rate constant on temperature

$$k' = A \exp(-E/RT) \text{ over the range } 400^\circ\text{C to } 600^\circ\text{C}$$

where

$$E = 12 \text{ kJ/mole and } A = 0.14 \text{ % Ce s}^{-1}\text{kPa}^{-1}.$$

Notation

- a = initial concentration of reactant
A = frequency factor
 a_c = initial concentration of cerium on the sorbent
E = activation energy
k = general rate constant
 k' = rate constant calculated from Equation 7
m = reaction order with respect to fractional unreacted cerium oxide on the sorbent
n = reaction order with respect to partial pressure of SO_2
 P_s = partial pressure of SO_2
r = rate of consumption of cerium oxide
R = gas constant
t = time
T = absolute temperature
x = concentration of reactant that has been consumed at time = t
 x_c = concentration of cerium oxide that has been consumed at time = t

Disclaimer

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not imply endorsement or favoring by the United States Department of Energy.

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Pharmaceutical Wastewater Treatment Comparison Of Process Scale-up From Bench to Full-Scale: A Case Study

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Wastewater treatability investigations were conducted for a specialty batch pharmaceuticals production facility which typically produces small quantities of numerous chemicals and pharmaceuticals. Production campaigns typically range from two days to four weeks in duration. Due to these production changes, the organic loading and chemical makeup of the wastewater constantly varies, resulting in less than optimum treatment plant performance. In addition, the facility planned to increase production in the future, thereby increasing wastewater flow and organic load.

Introduction

Wastewater was biologically pretreated at the facility prior to discharge to the local Publicly Owned Treatment Works (POTW). A new pretreatment discharge permit went into effect in January 1988 with the following instantaneous maximum discharge limits:

BOD	-	300 mg/l
TSS	-	300 mg/l
COD	-	1,000 mg/l
Oil and Grease	-	100 mg/l
Cyanide	-	33.5 mg/l

The existing wastewater treatment facility was not capable of consistently achieving these discharge limitations at the existing flow condition and would also be incapable of

achieving these treatment levels with the intended increase in production.

An investigative program was conducted to determine system upgrading requirements to ensure future compliance with these new discharge limitations. The project was conducted in three phases:

- Phase I - Process Investigations
- Phase II - Wastewater Treatment & Facilities Modifications
- Phase III - Plant Start-up

This paper summarizes the results of the process investigations and definition phases and compares predicted plant performance based on treatability studies to actual plant performance during 21 months following implementation of the recommended modifications.

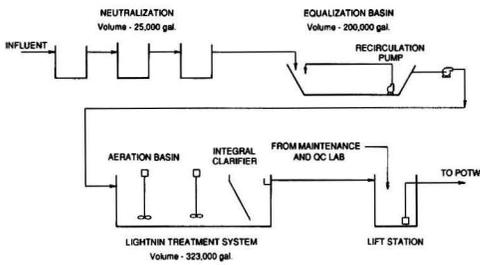


FIGURE 1. Existing wastewater treatment system process flow diagram.

Phase 1 - Process Investigations

Existing Wastewater Treatment Facility

Wastewater is generated from various production areas as a result of washdown, blowdown, and general house-keeping activities. The existing wastewater treatment facility (WWTF) was designed for pretreatment of the production plant wastewaters prior to discharge to the local POTW. The facility consisted of neutralization, equalization, and biological treatment. A process flow diagram of the system is presented in Figure 1 with associated design criteria presented in Table 1.

Treated effluent from the clarifier flowed to a manhole where domestic sewage and other lightly contaminated wastestreams (such as maintenance and laboratory washwaters) from the facility entered and were combined to form the final effluent used for discharge monitoring purposes. Therefore, treatment of the process wastewater to below the permit limits was required due to the contribution of the sanitary and other miscellaneous wastestreams to the total effluent.

Historical Data Evaluation

An evaluation of historical wastewater facility data was performed to determine any significant events, correlations, or trends which could be useful for wastewater treatability studies and process design. Various parameters and relationships, i.e., temperature variations, pH fluctuations, wastewater variability, and nondegradable COD, were developed in an attempt to isolate factors which could be causing poor plant performance.

The data review indicated that aeration basins temperatures ranged from approximately 18°C in winter to 40°C in summer, with a corresponding effect on the specific organic removal rate. The high summer temperatures were due to the high organic strength of the wastewater in combination with a consistent two-foot foam layer on the aeration basin surface which provided excellent insulating properties.

The data also indicated there were substantial pH swings in the aeration basin contents which were attributed to pH

controller problems and short circuiting in the upstream equalization basin. The short circuiting in the equalization basin also contributed to increased aeration basin effluent variability. Analysis of BOD and COD data indicated that the minimum achievable effluent COD was approximately 1,100 mg/l with complete BOD removal, with the effluent COD varying from 1100 to 5,000 mg/l. The implications of these data are that there is a minimum concentration of effluent COD which can be achieved through biological treatment alone and that this COD level will on the average be greater than the permit limitation of 1,000 mg/l. Therefore, to consistently achieve the permit limits, supplemental treatment would be required. Upgrading possibilities included pretreatment to enhance biodegradability and/or post-treatment for removal of residual COD.

Table 1 - Existing WWTF Process Design Summary

Neutralization

Flow	25,000 gpd
Volume	25,000 gal
HRT	1 day
Chemicals	NaOH, H ₂ SO ₄
pH	7.0-7.5
Stages	3

Equalization

Flow	25,000 gpd
Volume	189,000 gal
Type	In-ground, concrete/asphalt
HRT	7.5 days
Mixing	72,000 gpd recirculation pump

Biological Treatment

Flow Rate	25,000 gpd
Influent BOD (avg)	8,000 mg/l
Influent COD (avg)	12,000 mg/l
Volume	323,000 gal
HRT	13 days
Clarifier	Integral
Aeration	
Mixers (2)	2 speed, 20 HP ea
Blowers (2)	15 HP ea
Sludge Holding (2 tanks)	15,000 gal ea

Metric Units Conversion Factors:

gpd x 0.03785 = m ³ /day
gal x 0.03785 = m ³
horsepower x 745.69 = Watts

Process Screening Evaluations

In view of the historical data evaluation results that indicated high refractory COD levels in the biological plant effluent, several processes, including adsorption, chemical oxidation, and coagulation/precipitation, were screened for applicability. Chemical oxidation and coagulation/precipitation alone were found to provide inconsistent results due to the highly variable nature of the wastewater and were therefore not considered for further evaluation. As a result of these screenings, further investigative efforts were concentrated on the following treatment process train: neutralization, equalization, activated sludge, sand filtration, and granular activated carbon (GAC) adsorption.

Wastewater Variability Dampening

The original equalization basin (EQB) had a nominal operating volume of approximately 189,000 gal (715 m³). The EQB was unmixed except for a 72,000 gpd (272 m³/day) recirculation pump which transferred basin contents from the northwest corner of the EQB to the southeast corner thus providing a basin turnover rate of approximately once every 2.8 days. Based on a review of the EQB effluent data, it was apparent that there was a high degree of short circuiting. For this reason, and due to concerns regarding basin construction, size and integrity, a new complete mix equalization tank was designed.

Based on the highly variable nature of the wastewater constituents, the selected design equalization basin effluent organic load variability was approximately ± 25 percent of the mean such that the organic loading to the biological treatment unit was relatively constant. At the design average flow rate of 40,000 gpd (151 m³/day), the required complete mix equalization volume to achieve 25 percent load variability in the equalization basin effluent would be 190,400 gal. (720 m³). The effluent variability of the existing equalization basin system with limited mixing was back-calculated from available data. This calculation showed an actual effluent variability of 42 percent over the same data collection period. Therefore, since the existing and new equalization system volumes were essentially the same, the addition of mixing alone would reduce EQB effluent variability by at least 17 percent. A new equalization tank was installed for replacement of the existing in-ground basin due to the need identified in Phase I to eliminate short circuiting and provide a more uniform feed for the aeration basin.

Bench-Scale Treatability Investigations

Based on the results of the preliminary screening tests, it was determined that activated sludge/activated carbon treatment offered the most cost-effective and reliable means of achieving the required treatment goals. The preliminary carbon adsorption tests indicated that activated

TABLE 2 - Treatability Study Summary^a

PARAMETER	Influent	Reactor#1	Reactor#2
Flow, l/day		1.20	2.61
HRT, day		16.7	7.7
Sludge Age, day		50	50
Biomass MLSS, mg/l		2,430	3,108
Biomass MLVSS, mg/l		2,054	2,555
COD ₅ , mg/l	10,207	1,992	2,067
Percent COD ₅ Removal, %		80	80
BOD ₅ , mg/l	5,734	57	119
Percent BOD ₅ Removal, %		99	98
TOC, mg/l	3,281	565	650
Percent TOC Removal, %		83	80
F/M, BOD Basis, day ⁻¹		0.17	0.29
F/M, COD Basis, day ⁻¹		0.30	0.52
Sludge Yield Factor, gMLVSS/g BOD Removed		0.20	0.19
SVI, ml/g		157	74
TSS ^b , mg/l		100-150	100-150
Biodegradable COD/BOD Ratio		1.4	1.4

^aValues presented are averages for the study period.

^bFollowing polymer addition and settling.

carbon alone could reduce biological treatment plant effluent COD to well below 1,000 mg/l on a consistent basis and the addition of a coagulation/filtration step prior to the carbon system would be required to reduce suspended solids in the carbon system influent.

The experimental design included operation of two bench-scale activated sludge reactors. Reactor 1 received the projected near term loading while Reactor 2 was designed to simulate the performance of the system under increased production conditions, that is, twice normal flow. It was assumed that the future waste strength would remain essentially the same as the current wastewater, but the wastewater volume would be doubled under increased production conditions. Results from Reactor 2 could then be compared to those from Reactor 1 to determine the actual capacity of the existing treatment facility and for definition of process requirements for increased capacity. Table 2 presents a summary of pertinent analytical results for the two reactors. Results for individual parameters of interest are discussed below.

Effluent COD

Reactors 1 and 2 achieved average effluent soluble COD (COD₅) values of 1,992 and 2,067 mg/l, respectively, with no significant statistical difference in performance. These results indicate that the existing facility should be capable of operating at twice the existing hydraulic and mass organic loadings while achieving essentially the same

effluent quality. Statistical analysis of the data did, however, indicate more variability in the Reactor 2 effluent with standard deviations of 257 mg/l and 519 mg/l for Reactors 1 and 2, respectively.

Effluent BOD

Reactor 1 and 2 effluent soluble BOD (BOD_5) averaged 57 and 119 mg/l, respectively. These results indicate that the residual COD in Reactor 1 is essentially all non-biodegradable material. Reactor 2 did not achieve the same level of BOD removal as Reactor 1 which is most likely attributable to the reduced HRT. The difference in effluent COD between Reactors 1 and 2 is essentially equal to the difference in effluent BOD assuming a biodegradable COD/BOD ratio of 1.4:1 (see Table 2). The difference in effluent BOD for Reactors 1 and 2 is 62 mg/l which yields an equivalent COD of 87 mg/l. If this is added to the Reactor 1 effluent COD of 1,992 mg/l, the resulting COD concentration of 2,079 mg/l is essentially equal to the 2,067 mg/l observed. This reaffirms that the effluent COD of Reactors 1 and 2 is primarily non-biodegradable and must be removed by other means such as carbon adsorption.

Sludge Production

Production of excess sludge is inherent to biological treatment systems with the amount of sludge production

dependent on operating conditions and substrate characteristics. Calculation of sludge production in each of the reactors was by mass balance. Table 2 shows that the sludge yield factors for Reactors 1 and 2 were 0.20 and 0.19 g MLVSS/g BOD removed, respectively. This value is within the expected range for systems operating at sludge ages near 50 days.

Sludge Settling

Sludge settling, as characterized by the sludge volume index (SVI) test, was evaluated. Results of these tests are given in Table 2 and indicate improved settling at the higher loading rate of Reactor 2. Effluent TSS concentrations following polymer addition indicate the facility would be in compliance with pretreatment effluent TSS limits. However, due to the need for granular activated carbon for removal of refractory COD, additional suspended solids removal consisting of sand filtration was required to prevent fouling of the GAC adsorption system.

Carbon Adsorption

Carbon adsorption tests on the reactor effluent were conducted by Calgon Corporation. The initial testing consisted of development of isotherms followed by accelerated column testing (ACT), and carbon reactivation evaluations. ACT testing indicated that the carbon usage rate based on an influent COD of approximately 2,400 mg/l

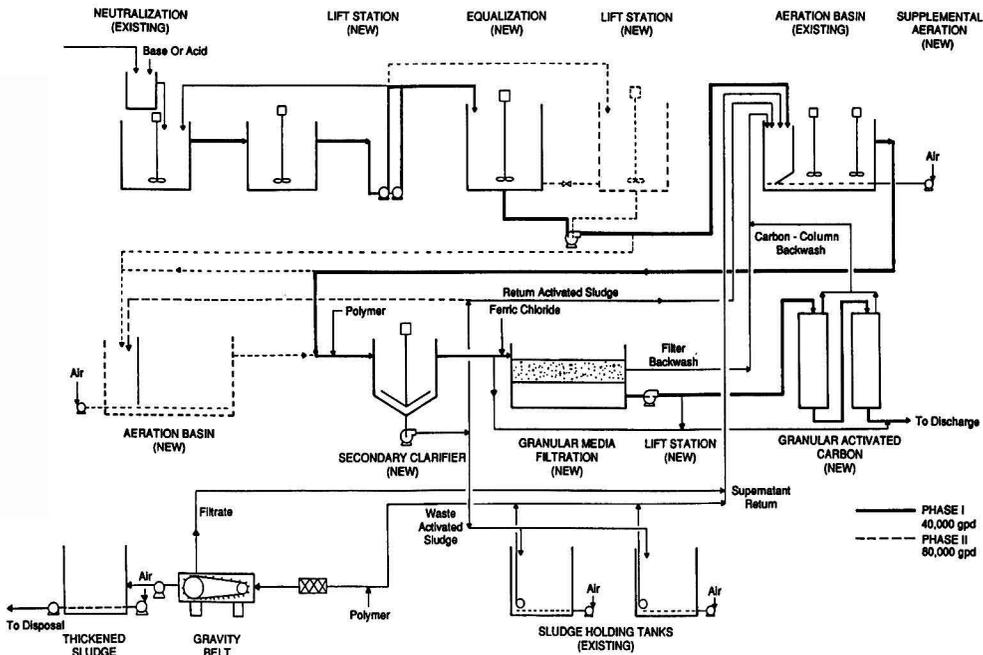


FIGURE 2. Modified wastewater treatment system process flow diagram

and effluent COD of 900 mg/l was 1.3 g carbon per g of COD removed.

Phase II - WWTF Modifications

A process flow diagram of the modified treatment system is presented in Figure 2. Specific information on equipment sizing is shown on Table 3. Raw wastewater enters the existing neutralization system for pH stabilization. Following pH neutralization, the wastewater is pumped to a new above-ground, completely mixed, 250,000 gal. (946 m³) equalization tank. The new tank was installed for replacement of the existing in-ground equalization basin due to potential regulatory requirements relating to surface impoundments. Provisions for a future tank were also included. The new equalization tank operates as a variable level, completely mixed tank.

Equalized wastewater is pumped at a relatively constant rate to the existing aeration basin. The aeration basin was modified such that the former integral clarifier now serves as a biological selector to improve sludge settling characteristics. A new 28-ft (8.53 m) diameter external secondary clarifier was installed. Additional aeration capacity was added to the existing aeration basin to accommodate flows up to 40,000 gpd (151 m³/day). (Provisions for a future aeration basin were also included.)

The aeration basin mixed liquor flows by gravity to the new external clarifier. Polymer is injected into a flash mix tank prior to the clarifier to enhance suspended solids separation. Settled sludge is returned to the biological selector via return activated sludge (RAS) pumps.

A portion of the RAS is wasted to either of two aerated sludge holding tanks. This waste sludge is then thickened in the sludge holding tanks by intermittently aerating and settling the sludge. The supernatant is returned to the biological selector. Further thickening with a gravity belt thickener substantially reduces the quantity of sludge for hauling to the final disposal site.

Following the secondary clarifier, the flow is directed to the sand filter (72 sq ft or 6.69 m² area) and granular activated carbon columns (two 10-ft. or 3.05m diameter units). Typically, 50 to 80 percent of the flow is treated in the GAC system with the remainder bypassing the GAC system and flowing to the discharge point for blending with the GAC treated flow. This mode of operation increases the carbon utilization efficiency by up to 50 percent since the anticipated effluent COD from the GAC system is typically less than 300 mg/l. The GAC treated effluent then combines with the biologically treated effluent from the sand filter which was not treated by the GAC system to provide a composite effluent COD within the 1,000 mg/l permit limit. If the discharge COD concentration from the carbon system or aeration basin changes, the percentage of flow treated by

Table 3 - System Expansion Design Conditions and Recommended Equipment Size

Neutralization (Existing)	
Flow	40,000 gpd
Volume	25,000 gal
HRT	15 hr
Chemicals	NaOH, H ₂ SO ₄
pH	7.0-7.5
Stages	3
Equalization (New)	
Flow	40,000 gpd
Volume	250,000 gal
Type	Above ground, completely mixed
HRT	3.1 day
Aeration Basin (Existing)	
Avg. Flow	40,000 gpd (29 gpm)
Influent COD	12,000 mg/l (4,000 lb/day)
Influent BOD	8,000 mg/l (2,668 lb/day)
Nondegradable COD	1,100 to 2,100 mg/l (370 to 634 lb/day)
Aeration Basin Volume	323,000 gal
HRT	8.1 days
Oxygen Requirements	190 lb/hr
Secondary Clarifier (New, Designed for 80,000 gpd flow)	
Type	Circular, center feed, flocculation, peripheral launder
Diameter	28 ft
Surface Area	450 sq ft
Hydraulic Loading	180 gpd/ft ² at 80,000 gpd
Granular Media Filter (New, Designed for 80,000 gpd flow)	
Type	Gravity, automatic backwash, shallow bed
Size	72 sq ft ±
Hydraulic Loading	0.8 gpm/sq ft at 80,000 gpd
Granular Activated Carbon Adsorption System (New, Designed for 80,000 gpd flow)	
Type	Downflow, pressure carbon columns, series or parallel operation
Size	2 each 10 ft Ø adsorbers
Capacity	20,000 lb carbon/adsorber

Table 3 (continued) - System Expansion Design Conditions and Recommended Equipment Size

Backwash Flow Capacity	Manual backwash system >80,000 gpd
Gravity Belt Thickener (New, Designed for 80,000 gpd flow)	
Type	Continuous belt, gravity type
Capacity	50 gpm max; 25 gpm avg
Influent TSS	1.5 to 2.5 percent
Thickened Solids	5 to 7.5 percent
Polymer Addition	Integral to system

Metric Units Conversion Factors:

- gpd x 0.03785 = m³/day
- gal x 0.03785 = m³
- lb/day x 0.4536 = kg/day
- gpm x 0.03785 = m³/min
- lb/hr x 0.4536 = kg/hr
- ft x 0.304 = m
- ft² x 0.0929 = m²
- gpd/ft² x 0.0035 = m³/day/m²
- gpm/ft² x 0.0035 = m³/day/m²
- lb x 0.4536 = kg

the carbon is changed accordingly. The carbon system is sized to accept the entire future flow rate of 80,000 gpd (303 m³/day).

Comparison Of Predicted And Actual Plant Performance

Data collected from the modified WWTF over a period of 21 months were evaluated for comparison to the data collected during the bench-scale treatability program. Table 4 presents the monthly average summary data from the modified full-scale WWTF for the 21-month evaluation period for parameters of interest. Table 5 presents a comparison of key operational and performance parameters from the bench-scale studies and the 21 month full-scale operating period.

Equalization System Comparison

The performance of the full-scale equalization basin can be evaluated by comparing the actual effluent variability (COD basis) to that predicted for design based on the method developed by Novotny and Englande [1]. The equalization basin design was based on data from a three-per-week sampling schedule and included some assumptions and manipulation of data to reflect expected wastewater characteristics. The results of the equalization analysis predicted the equalization basin effluent COD variability as a percent of the mean COD loading would be ±25 percent with a 95 percent confidence limit. Actual plant operating data indicate the average variability was 33 percent of the mean loading with a 95 percent confidence limit over the course of the 21 month evaluation period. The actual variability of the equalization basin effluent was

Table 4 - Wastewater Treatment Plant Operation Data for April 1989 Through December 1990 Period

Equalization Tank Effluent					Aeration Tank			Aeration Tank Effluent		GAC Columns					
Year	Month	Flow (gpd)	Average COD (mg/l)	COD Variability (% of Mean)	F/M (g COD/g MLVSS/day)	SVI (ml/g)	COD Removal (%)	CODs (mg/l)	TSS (mg/l)	Influent GAC Flow (gpd)	Percent Total Flow Treated (%)	Influent COD (mg/l)	Effluent COD (mg/l)	COD Removed (lb/mth)	Total Effluent COD (mg/l)
89	4	42,600	7,701	24	0.24	-	89.0	850	49	35,915	0.84	894	346	4,924	432
89	4	40,435	7,987	40	0.15	-	86.9	1,048	230	36,503	0.90	1,367	534	7,861	615
89	6	44,231	8,330	19	0.15	-	90.6	781	190	36,891	0.83	969	276	6,396	391
89	7	38,363	9,767	35	0.15	-	87.3	1,241	146	24,936	0.65	1,414	334	6,963	712
89	8	32,801	5,363	82	0.11	-	77.2	1,225	89	19,059	0.58	1,325	270	5,198	712
89	9	40,711	6,884	20	0.12	-	82.4	521	31	28,059	0.69	868	169	2,801	293
89	10	44,831	9,034	34	0.18	66	90.0	905	37	32,434	0.73	944	263	5,710	448
89	11	42,566	9,908	30	0.23	79	85.8	1,408	122	34,983	0.82	1,525	290	10,810	510
90	12	35,433	13,641	27	0.28	78	91.4	1,187	143	30,615	0.86	1,269	541	5,762	640
90	1	32,726	11,823	25	0.20	71	88.6	1,327	138	27,685	0.85	1,508	495	7,251	651
90	2	42,723	9,140	16	0.21	64	85.9	1,291	49	27,066	0.63	1,344	419	5,846	758
90	3	44,910	10,201	20	0.23	80	89.2	1,097	81	34,086	0.76	1,142	474	5,897	535
90	4	45,847	9,572	27	0.23	77	88.4	1,111	56	21,062	0.46	1,189	307	4,542	773
90	5	43,872	8,798	27	0.23	83	89.4	935	70	26,167	0.60	1,014	283	4,945	578
90	6	44,298	6,972	30	0.21	57	85.4	1,018	62	21,914	0.49	987	326	3,624	660
90	7	42,602	6,997	39	0.20	66	92.9	494	18	19,330	0.46	489	183	1,563	348
90	8	30,708	5,695	91	0.15	95	93.0	397	15	18,179	0.59	300	50	1,175	152
90	9	39,197	9,694	39	0.31	84	95.5	440	20	27,086	0.69	486	86	2,704	209
90	10	38,552	11,338	27	0.27	86	93.5	740	17	30,650	0.80	787	104	5,412	244
90	11	38,972	9,230	22	0.26	117	91.9	752	12	21,312	0.55	776	124	3,471	419
90	12	39,866	8,789	30	0.23	116	93.7	552	19	30,237	0.76	621	178	3,463	285
AVERAGE		40,281	8,884	33	0.21	82	89.4	919	75	27,832	0.69	956	288	5,062	498

Metric Units Conversion Factors:
 gpd x 0.003785 = m³/day
 lb/month x 0.4535 = kg/month

8 percent higher than that predicted from the process design and is attributed to the assumptions required in the data evaluation phase and to changes in production since the wastewater investigations were conducted. This small increase in variability from the predicted design value is not considered significant and should not impact biological treatment system performance.

Activated Sludge System Comparison

Comparative data from the bench-scale studies and the 21-month full-scale operation evaluation period are shown on Table 5. Data for aeration basin effluent COD, SVI, and secondary clarifier effluent TSS are shown on Figures 3, 4 and 5, respectively.

The full-scale operating data indicate the average flow to the aeration basin was essentially the same as the basis of design of 40,000 gpd (151 m³/day). However, the average influent COD to the aeration basin was 8,884 mg/l in contrast to the predicted design value of 11,700 mg/l. The reduced loading may be attributable to source reductions in the production area. As a result of the reduced organic loading, the full-scale F/M ratio (COD basis) was 0.21 day⁻¹ as compared to the design value of 0.30 day⁻¹. This reduced loading resulted in an improvement in biological treatment performance.

Wastewater biodegradability can be compared on the basis of the organic removal rate constant (K) as follows [2],

$$\frac{(S_o - y)(S_o - S_e)}{X_v t} = K(S_e - y) \quad (1)$$

Where: S_o = influent substrate concentration
 S_e = effluent substrate concentration
 y = nonbiodegradable substrate concentration
 X_v = aeration basin MLVSS concentration
 t = hydraulic residence time

The K rate developed from the bench-scale studies was 14.5 day⁻¹ at 22°C. If this K rate is used to evaluate data from the full-scale plant, the results indicate the effluent nondegradable COD would be 862 mg/l with a degradable COD of 96 mg/l for a total average effluent COD concentration of 958 mg/l. No BOD data were collected on the full-scale aeration basin effluent, however, assuming a COD/BOD ratio of 1.4, the effluent BOD would be approximately 69 mg/l which is consistent with the bench-scale treatability results.

The observed average activated sludge system effluent COD value was 919 mg/l during the 21-month operating period compared to 2,000 mg/l predicted from the bench-scale studies. However, when all actual average operational parameters are accounted for (that is, actual HRT, MLVSS, temperature, and substrate concentration), use of Eq. 1 as described above yielded a predicted effluent COD value of 958 mg/l using the bench-scale K rate value which checks closely with the actual observed value of 919 mg/l. The

TABLE 5 - Comparison of Predicted and Actual Plant Performance

PARAMETER	DESIGN BASIS ^a	ACTUAL
Flow, gpd	40,000	40,300
EQB Effluent Variability (± % of mean)	25%	33%
Influent COD, mg/l	11,700	8,884
MLVSS, mg/l	5,000	5,764
HRT, days	8.0	8.0
COD _r Removal, %	80.0	89.4
Aeration Tank Effluent COD, mg/l	2,000, (958 ^b)	919
SVI, ml/g	157	82
Secondary Effluent TSS, mg/l	150 max	75 avg
F/M, COD Basis, day ⁻¹	0.30	0.21
Sludge Yield, g MLVSS/g BOD Removed	0.20	0.34
Sludge Age, day	50.0	29.6
K, day ⁻¹	14.5	14.5
Carbon Usage Rate, g GAC/g COD Removed	1.30	1.74
GAC Bypass Rate, %	20.0	30
Oxygen utilization, g O ₂ /g COD Removed	0.80	0.62
Temperature, °C	20.0	28.5

^a Based on bench-scale data and projected operating conditions.

^b Corrected for actual average operating conditions of flow, influent COD, MLVSS, HRT, and temperature using Eq 1.

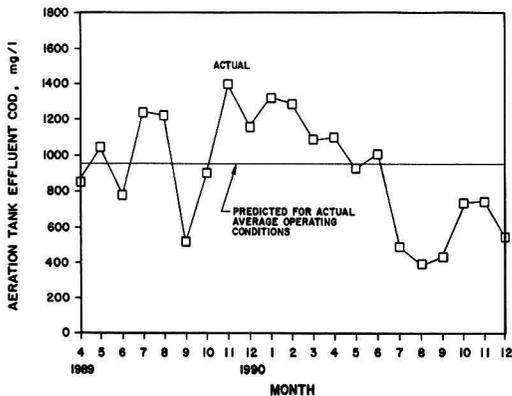


FIGURE 3. Aeration tank effluent soluble COD.

changes in production at the plant appear to have resulted in a reduction of the nondegradable portion of the COD as reflected by the effluent COD data.

Over the 21-month period the sludge yield coefficient averaged 0.34 g MLVSS/g BOD removed, with a sludge age of 29.5 days. This yield value is in reasonable agreement with the 0.20 g MLVSS/g BOD removed that was predicted by the bench-scale study when sludge age was controlled at 50 days. The following equation can be used to compare plant and bench-scale study conditions [3]:

$$Y_t = Y_{obs} \cdot (1 + q \cdot K_d) \quad (2)$$

Where: Y_{obs} = observed yield, lb MLVSS/lb BOD removed
 Y_t = true yield, lb MLVSS/lb BOD removed

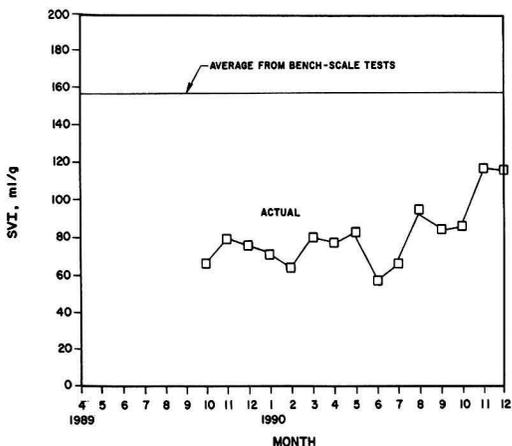


FIGURE 4. Sludge volume index.

q = sludge age, day
 K_d = endogenous decay coefficient, day⁻¹

Using a typical K_d value of 0.05 day⁻¹, the resulting Y_t values for the bench and full-scale conditions are 0.70 and 0.84, respectively. It is likely that the increased mixing in the new equalization tank resulted in an increase in aeration basin influent TSS and VSS concentrations, thereby resulting in the observed increase in sludge yield.

The oxygen requirement developed from the bench-scale studies was 0.80 mg O₂/mg COD removed. The average actual observed oxygen requirement was 0.62 mg O₂/mg COD removed in the plant. This lower value; however, is consistent with the lower operational sludge age (29.5 days vs. 50 days in the bench-scale study) and the higher sludge yield coefficient. Thus, during full-scale plant operation more COD was channelled into cell synthesis with a resulting decrease in the oxygen consumption per unit weight of COD removed. Using the sludge yield coefficients obtained from the bench-scale study (0.20 g MLVSS/g BOD removed) and the full-scale plant operation (0.34 g MLVSS/g BOD removed), it can be shown that the oxygen requirement corresponding to a yield of 0.34 lb MLVSS/lb BOD removed would correspond to 0.66 mg O₂/mg COD removed. This compares well with the measured value of 0.62 mg O₂/mg COD removed in the full-scale plant operations. This comparison is based on the following relationship:

$$COD_{removed} = COD_{respired} + COD_{synthesized} \quad (3)$$

Therefore, for 1 mg of COD removed, the bench-scale studies yielded a COD respiration of 0.8 mg O₂/mg COD removed and a cell yield of 0.2 mg MLVSS/mg BOD removed. Assuming a COD to BOD ratio of 1.4 and

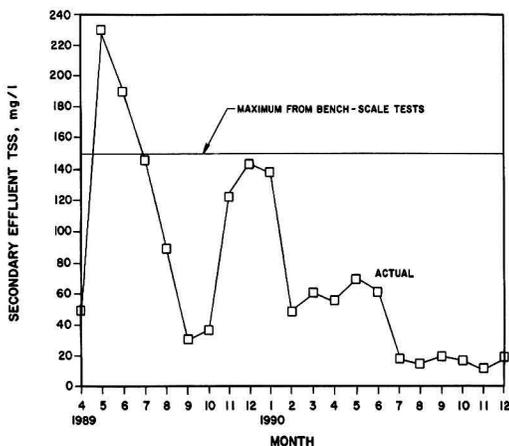


FIGURE 5. Secondary clarifier effluent TSS.

a COD equivalent for MLVSS of 1.4 mg COD, the balance shown in Eq. 3 checks at 1 mg O₂/mg COD removed. Using this same approach, the full-scale plant data balance within 4 percent of the theoretical value:

$$\begin{aligned} &1.0 \text{ mg COD}_{\text{removed}} @ 0.62 \text{ mg O}_2/\text{mg COD}_{\text{removed}} \\ &+ 0.34 \text{ mg MLVSS}/\text{mg BOD}_{\text{removed}} \\ &1.0 \text{ mg COD}_{\text{removed}} @ 0.96 \text{ mg O}_2 \end{aligned}$$

A chronological comparison of the aeration basin effluent COD over the 21-month evaluation period to the predicted value is shown in Figure 3. As indicated by the average aeration basin effluent COD value of 919 mg/l as compared to the design value of 2,000 mg/l, the full-scale plant performed better than predicted; however, this improved performance is largely attributable to the reduced organic loading during the 21-month evaluation period. This is supported by the K rate comparison discussed previously and an associated reduction in non-degradable COD.

Sludge settling characteristics (Figure 4) and effluent TSS values (Figure 5) from the 21-month full-scale evaluation period were also better than predicted. The effluent TSS values from the plant indicate periods of upset associated with the plant start-up followed by a general improvement over time. The clarifier effluent suspended solids averaged approximately 20 mg/l over the last six months of the evaluation period reflecting stabilized system operation and polymer optimization. The data also indicate that bench-scale test data may not provide an accurate quantification of solids/liquid separation performance as reflected by the greatly reduced effluent TSS concentrations over the last six months of plant operation as compared to the predicted bench-scale results.

Granular Activated Carbon System

The GAC system installed at the facility was designed to provide sufficient capacity for the future plant expansion flow condition of 80,000 gpd (303 m³/day). As can be seen from the design data in Table 3, the GAC system is lightly loaded on a hydraulic basis. The primary parameter of concern from an operational standpoint with GAC is the carbon utilization rate. Process definition information developed by Calgon Corporation indicated a carbon utilization rate of 1.3 g carbon/g COD removed at an influent COD concentration of 2,400 mg/l. As described previously, the actual aeration basin effluent COD (GAC influent COD) was 919 mg/l. Since adsorption is a concentration dependent process, the reduced driving force resulting

from the lower influent COD concentration would be expected to result in an increase in carbon utilization rate on mass per mass basis. Operational data over the 21-month evaluation period indicate the actual carbon utilization rate was 1.74 g carbon per g of COD removed which appears to be consistent with the reduced influent COD concentration.

The full-scale treatment facility bypassed approximately 30 percent of the wastewater flow around the GAC system due to the low COD concentrations in the activated sludge effluent. The remainder of the flow was maintained through the GAC system, even though on average it was within permit limits, to provide a buffer in the event of activated sludge effluent variability which could result in permit excursions. The original design anticipated a bypass rate of approximately 20 percent of the flow based on treatability test results.

Conclusions

Bench-scale treatability studies are a cost-effective means to develop process definition and design criteria for wastewater treatment applications. Bench-scale testing can provide an excellent predictive tool for developing process design criteria such as oxygen utilization, sludge production, and specific organic removal rates, and for projecting treatment process performance, provided the wastewater used in the testing is representative of the full-scale system.

Results of this case study indicate that the full-scale treatment system provided similar treatment operation and performance as projected by the bench-scale studies after differences in wastewater organic loading between the bench- and full-scale systems are accounted for. The use of representative wastewater samples in the bench-scale phase is the single most important factor in obtaining representative performance and design information.

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Integrated Anaerobic-Aerobic Process for the Biodegradation of Chlorinated Aromatic Compounds

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*An integrated anaerobic-aerobic process for the complete mineralization of 2,4,6-trichlorophenol (used in this work as the model toxic halogenated aromatic compound to degrade) was successfully tested and operated. The sludge obtained from the anaerobic digester of a commercial treatment plant was used to obtain an anaerobic consortium capable of partially dechlorinating 2,4,6-trichlorophenol (2,4,6-TCP). The clarified and sterilized effluent from the same anaerobic digester was used as the medium for the anaerobic consortium. During the anaerobic process 2,4,6-TCP was first dechlorinated to 2,4-dichlorophenol and then to 4-chlorophenol (4-CP). Stoichiometric amounts of 4-CP were recovered. Similar results were obtained when the anaerobic microorganisms were immobilized on Manville R-635 silica beads. After immobilization, the consortium was able to dechlorinate 150 μM of 2,4,6-TCP in four days. *Pseudomonas Glathei* and an indigenous culture obtained from same sludge used to produce the anaerobic enrichment culture were shown to be able to degrade the 4-CP produced from the anaerobic dechlorination of 2,4,6-TCP. However, for the aerobic 4-CP mineralization to occur the medium had to be buffered with phosphate, since high pH would inhibit the aerobic bacterial activity. It is expected that the proposed approach will be used to treat recalcitrant halogenated compounds that are not amenable to conventional biological treatment.*

Introduction

The biological treatment of wastewaters containing low concentrations of pollutants is typically one of the most efficient and cost-effective waste treatment technologies available to industry. However, as waste contaminants become more toxic and recalcitrant, the commonly used technology of employing well aerated tanks containing an acclimated mixed population may no longer be successful. It is becoming increasingly evident that a more sophisticated approach is required to treat such complex wastes as streams contaminated with halogenated aromatic compounds [1, 2, 3]. In particular, it has been found that multihalogenated aromatic compounds can be very recalcitrant

to dehalogenation and mineralization by aerobic microorganisms. In addition, the compound recalcitrance appears to increase proportionally with the number of halogen atoms on the molecule, and to be affected by their position [4].

However, it has also been shown that anaerobic microorganisms have great potential for attacking these multihalogenated compounds by means of reductive dehalogenation [5, 6, 7, 8, 9]. In addition, their ability to dehalogenate typically increases with the level of halogenation of the molecule. These factors make the possibility of using anaerobic microorganisms in hazardous waste treatment very attractive. However, a major drawback of the use of these microorganisms is in their difficulty to completely mineralize the partially dehalogenated com-

pounds produced in the process. Aerobic microorganisms, on the other hand, have been successfully used in the past to attack and completely mineralize many non-halogenated (or only lightly halogenated) compounds [1, 10, 11]. This indicates that the potential exists for treating halogenated organic molecules using a sequential, two-step, anaerobic-aerobic treatment process, in which anaerobic dehalogenation is followed by complete aerobic mineralization.

Therefore, the objective of this work is precisely to study such a process in which an integrated anaerobic-aerobic system is used to degrade a model toxic compound, that is, 2,4,6-trichlorophenol, as well as its reductive dechlorination products.

Previous Literature on Anaerobic-Aerobic Biological Treatment and Related Processes

The literature in this area has been reviewed by Reineke and Knackmuss, [4] and Muller and Lingens [12] for the anaerobic case, and by Chaudhry and Chapalamadagu, [1] and Gibson [13] for the aerobic case. However, only a very limited number of references can be obtained for the case of a combined anaerobic-aerobic treatment process. Pioneering work was carried out by Salkinoja-Salonen and co-workers on the use of a two-stage reactor system for the treatment of waste effluents from paper pulp bleaching plants [14, 15]. In these studies, the overall removal of the pollutants of interest (typically mixtures of chlorophenols) was reported, but the extent of biodegradation due to each system was not determined.

An anaerobic-aerobic treatment process was also investigated by Slonim et al. [16] for the removal of 4,6-dinitro-cresol from wastewater using an anaerobic recycle fluidized bed reactor followed by an aerobic activated sludge reactor to mineralize the compound. Dienemann et al. [17] have reported the use of serial anaerobic-aerobic reactors packed with soil and sand to treat a Superfund site leachate containing high levels of Total Organic Carbon (TOC) but no pesticides, Polychlorinated Biphenyls (PCBs) or other halogenated organics. High carbon removal rates were observed. Collivignarelli et al. [18] recently presented results for an anaerobic-aerobic industrial pilot plant for the treatment of municipal wastewaters. The emphasis of this work was on the removal of Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), and nitrogen from wastewaters, and not on the treatment of hazardous substances.

In a recent patent [19] an anaerobic-aerobic treatment process (Zimpro/Passavant, Inc.) was also described, in which the majority of COD was removed in the anaerobic step, and further wastewater purification was achieved by biophysical aerobic treatment. The aerobic degradation was carried out in a reactor also containing powdered activated carbon particles in suspension. This patent is based on other recent patents which also utilized activated carbon in conjunction with anaerobic microorganisms [20], or aero-

bic bacteria [21]. The combined use of activated carbon and biological degradation activity is a key aspect of the PACT® treatment process [22] which is currently used in many industrial facilities, such as the DuPont Deepwater, NJ, facility [23].

All these recent studies focused on anaerobic-aerobic treatment (many of them industrial applications) clearly demonstrate the potential use and industrial interest for this kind of process. However, the majority of the studies reported above show that these processes are primarily focused on the treatment of wastewaters containing high levels of TOC, and not on the use of the specific degradation capabilities of each class of microorganisms (anaerobic vs. aerobic) to attack and eventually mineralize halogenated organic toxic compounds. By contrast, this is one of the key features of the process described in this work.

Apparatus, Materials, and Procedures

Inocula, Media, and Buffer Solution Preparation

Anaerobic enrichment cultures were established in serum bottles (as explained below) in the presence of 2,4,6-trichlorophenol, using samples taken from anaerobic digesters of two local sewage treatment plants, that is, the Livingston (NJ) Sewage Treatment Plant, and the Joint Meeting Sewage Disposal Commission facility in Elizabeth (NJ). The enrichment cultures served as inocula for all the anaerobic as well as the aerobic systems used in this work. This implies that the aerobes (or facultative anaerobes) present in the anaerobic cultures could survive under anaerobic conditions for a significant period of time. The aerobic cultures were selected from the start for degraders of 4-chlorophenol since this was expected to be the final product of the anaerobic dechlorination of 2,4,6-trichlorophenol. In addition, ATCC culture # 29195 (*Pseudomonas Glathei*) was also tested as a possible source of inoculum.

The medium used for both the anaerobic and the aerobic processes was obtained by autoclaving for 20 minutes at 121°C, and diluting 1:1 with deionized water the liquor taken from one of the above mentioned treatment plants. After settling overnight, the supernatant was removed, and centrifuged or filtered to remove any remaining solids. The COD of the final medium was measured by dichromate digestion at 150°C, and was found to be 500 mg/l. When the medium was used for the anaerobic process 2,4,6-trichlorophenol and resazurin dye, as an oxygen indicator, were also added. Then, the solution was autoclaved again. When the anaerobic experiments were first started, a mixture of Cysteine·HCl and Na₂S·9H₂O (0.025% of each), typically used for the most stringent anaerobes, was employed as the reducing agent. However, it was later found that the consortia adapted to the environment so well that the reducing agent was not needed in the medium.

When the medium was used for the aerobic cultures 4-chlorophenol was added. A second type of aerobic medium

was also used, namely the supernatant from the anaerobic cultures after the anaerobic dechlorination of 2,4,6-trichlorophenol to 4-chlorophenol was complete. This medium, containing the dechlorination products of the anaerobic process, had a pH that was too high for the aerobic cultures. Therefore, a phosphate buffer solution was added. KH_2PO_4 (monobasic) and Na_2HPO_4 (dibasic) were used to prepare buffer solutions. The concentration of the stock phosphate buffer was 1 M at the beginning of the project, but it was later changed to 0.5 M because of the difficulty in preparing 1 M Na_2HPO_4 solutions. A stock solution of pH 6.8 was used throughout the project to dilute the aerobic culture medium, when appropriate.

Analytical Determination of Chlorophenols

2-chlorophenol (2-CP), 3-chlorophenol (3-CP), and 2,6-dichlorophenol (2,6-DCP), were obtained from Aldrich Chemical Company, and 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-CP), and 2,4,6-trichlorophenol (2,4,6-TCP) from Sigma Chemical Company. 2,500 ppm stock solutions for each of these compounds were prepared in 0.1 N NaOH. Some of these compounds (such as 2,4,6-TCP or 4-CP) were directly tested for degradation during the experiments. Others (such as 2-CP or 3-CP) were only used to identify the possible reaction products of the biological degradation processes.

The samples taken from any of the serum bottles or reactors were stored at -20°C . After thawing, each sample was centrifuged, and the supernatant was acidified with acetic acid, aspirated into a syringe, and passed through a 13 mm x 20 μm filter unit containing filter paper for High Performance Liquid Chromatograph (HPLC) samples (Gelman Science). Sample volumes of 25 μl were injected into an HPLC Waters Component System, consisting of a Waters 600E System Controller, a Waters Model U6K universal liquid chromatograph injector (which was later replaced by a Waters 715 Ultra Wisp Sample Processor) and a Waters 484 Tunable Absorbance Detector. The column used was an Alltech Econosphere C8 5U 4.6 mm i.d. x 150 mm. An Alltech Direct Connect Refillable Guard Column filled with Guard Column Refill Pell. C8 was employed to protect the column. Mobile Phase A (1% acetic acid in methanol) and Mobile Phase B (1% acetic acid in Milli-Q Water), 50:50, were run isocratically. The flow rate was 1 ml/min. UV detection was at 280 nm, 0.5 AUFS. The data were processed by PE Nelson chromatography software (rev. 5.10) interfaced with 760 series Model 2600 data acquisition unit. The system was calibrated using solutions of known concentrations of 2,4,6-TCP, and its anaerobic metabolites, 2,4-DCP, 4-CP and phenol. The degradation products of the biological processes were first identified by comparison with the retention times of the known standards in the HPLC. The results were further confirmed by comparing the UV spectra of the dechlorination products with those of the standards.

Experiments with the Anaerobic Cultures

Initially, the anaerobic experiments were performed in 125-ml serum bottles. The bottles were filled under nitrogen with medium, anaerobic inoculum, 2,4,6-TCP (typically 100 μM), and resazurin (0.0001%), sealed with a butyl rubber stopper and an aluminum crimp seal, and incubated in the dark at 30°C . Samples were taken by inserting a syringe needle through the rubber stopper. Successive spikings of 2,4,6-TCP were made by syringe injection through the rubber stopper. In a second series of experiments in serum bottles, different aliquots of 1 M phosphate buffer solutions were added to bottles containing anaerobic mixed cultures in which 2,4,6-TCP dechlorination to 4-CP had been observed. The final concentrations of phosphate were equal to 0, 50, 100 and 150 mM, respectively. These bottles were additionally spiked with 2,4,6-TCP to assess the effect of the phosphate concentration on 2,4,6-TCP degradation.

A series of experiments were conducted in the recirculation reactor system shown in Figure 1a. The reactor was a Lucite cylinder, 5.08 cm in diameter and 20.3 cm high, provided with an inlet port located 1.5 cm above the bottom and an outlet port 1.5 cm below the top. The reactor was filled with porous silica cylindrical beads (Manville Celite Catalyst Carrier, R-635), roughly 3 mm in diameter and 5 mm in height. A screen supporting the beads was located above the inlet point. The reactor outlet was connected to a 250 ml storage flask, with a working volume of approximately 100 ml. The storage flask was also connected to a flask full of water, for the release of gases produced by the microorganisms. The outlet from the storage flask was connected back to the bottom of a reactor via a peristaltic pump (Pharmacia Fine, Model P-3). Only rubber tubing was used. Other types of tubing like PVC or tygon were found to be subject to oxygen permeation. The recirculation reactor system was filled with autoclaved medium and resazurin, under nitrogen. After inoculation, 2,4,6-TCP was added. The system was kept in the recirculation mode at all times. When the 2,4,6-TCP was completely depleted the system was spiked again. Additional anaerobic dechlorination batch experiments were carried out in the combined anaerobic-aerobic system, as described below in greater detail.

Experiments with the Aerobic Cultures

The aerobic batch mineralization process was conducted using 4-CP as target compound since previous experiments had shown that this was the final product of the anaerobic dechlorination reaction. The aerobic experiments were initially performed in 250 ml fernbach flasks with plastic caps. The working volume was 100 ml. Air was supplied by shaking the flasks in an incubator shaker. In the experiments with the ATCC culture # 29195 the organism was grown for three days in the medium made of sterilized

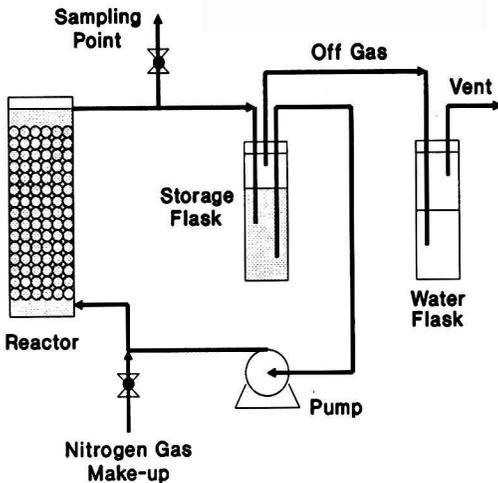


FIGURE 1a. Recirculated anaerobic reactor system.

supernatant from the treatment plant prior to adding 4-CP. Other aerobic batch experiments were carried out in the combined anaerobic-aerobic system, as described in the next section.

Experiments with the Anaerobic-Aerobic System

Anaerobic-Aerobic Batch System

The anaerobic component of this system consisted of a cylindrical Lucite batch reactor, 12.7 cm in diameter and 45.7 cm in height. The reactor was filled up with Manville Celite R-635 porous silica beads. Then, both ends of the reactor were sealed by rubber stoppers with glue and silicon rubber sealant. Because of the presence of the beads the void fraction in the reactor was 0.4 [24], and the volume of the liquid was 2.3 liters. The reactor was connected to a water reservoir creating a hydraulic seal to relieve the pressure buildup resulting from gas production. The reactor was filled up with the autoclaved medium containing 101.3 μM of 2,4,6-TCP and the inoculum. After a few days, a biofilm indicating microbial immobilization could be observed on the beads. Initially, the anaerobic reactor was operated under nitrogen to ensure that no oxygen was present in the system. This precaution was later found to be unnecessary, as determined by the color of the resazurin dye. Samples from the reactor were taken at different times to monitor the dechlorination of 2,4,6-TCP to 4-CP.

The aerobic component of the system was a cylindrical glass batch reactor, 10.4 cm in diameter and 40.7 cm in height, sealed with rubber stoppers. The working volume was approximately 1.9 liters due to the absence of packing. The aerobic step of the batch anaerobic-aerobic process consisted of transferring the content of the anaerobic reactor (upon completion of the anaerobic dechlorination process) to the aerobic reactor, and letting the indigenous

aerobic microorganisms present in the anaerobic culture attack the reaction product of the anaerobic step (4-CP). A 0.5 M phosphate buffer (pH 6.8) was also added in the ratio 1:4 to eliminate the negative impact of the high pH of the anaerobic solution on the aerobes. The aerobic culture was suspended in the medium by air bubbling (50 ml of air/min). The entire system was located in an environmental chamber kept at 30°C.

Anaerobic-Aerobic Continuous System

The components of this system were the same ones used in the anaerobic-aerobic batch system. However, the reactors were connected as shown in Figure 1b. All the liquids were pumped throughout the system via Micro Perspex two-channel peristaltic pumps (LKB Inc., Model 2132). The tubing for the pump was inspected every 100 hours and changed after 500 hours to minimize flow fluctuation due to worn tubing.

This system was started in batch mode with 2,4,6-TCP in the anaerobic reactor and 4-CP in the aerobic one. After the reactions were completed in both reactors, the continuous mode was started by opening the valves connecting the reactors, and feeding 20 ml/hr of a continuous sterile medium containing 2,4,6-TCP (231.9 μM) to the anaerobic reactor via a peristaltic pump. The flow direction in the anaerobic reactor was downward in order to minimize the channeling effect that had been observed in some preliminary experiments when the feed stream was fed to the bottom of the reactor. The output port of the anaerobic reactor was located approximately 5 cm above the reactor bottom and was provided with a T-connector for sampling purposes. Therefore, there were about 500 ml of dead reactor volume at the bottom of the reactor when the reactor was run in the continuous mode. This made the working liquid content of the reactor equal to 2.1 liters (as opposed to 2.3 liters in the batch mode).

The continuous aerobic reactor had a working volume of 2.15 liters. It received material from two sources: the

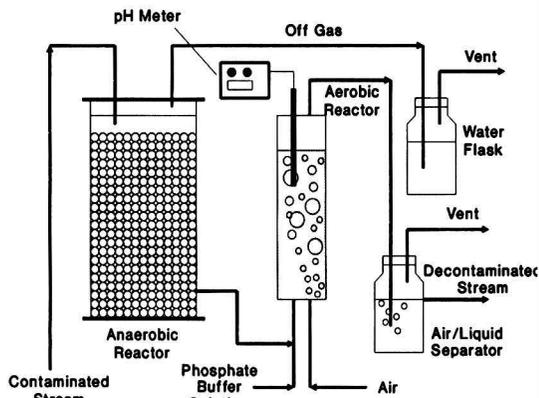


FIGURE 1b. Anaerobic-aerobic reactor system.

effluent from the anaerobic reactor (20 ml/hr), and a 0.5 M, pH 6.8 phosphate buffer solution. The flow rates of these two sources were in the ratio of 10:1, so that the final concentration of the phosphate buffer in the aerobic reactor was about 50 mM. A pH electrode was inserted through the top lid of the aerobic reactor to monitor the pH of the solution. The overflow from this reactor was collected to another reservoir operating as an air/liquid separator. The residence times for the anaerobic and aerobic reactors were 105 and 97.7 hours, respectively.

Results and Discussions

Anaerobic Dechlorination of Tri- and Dichlorophenols

The anaerobic dechlorination activity was first tested in the experiments conducted in serum bottles. The bottles were spiked with some 100 μM 2,4,6-TCP and the dechlorination reaction was followed as a function of time. Figure 2 shows the results. 2,4,6-TCP was dechlorinated in the process, and this reaction was accompanied by the production of 2,4-DCP, which was, in turn, reduced to 4-CP. Small amounts of phenol were also produced. The figure also reports the differential concentration of 4-CP, that is, the concentration of 4-CP minus the concentration of 4-CP at the time the new 2,4,6-TCP spiking was made. In this run, the initial 4-CP concentration was different from zero because of the accumulation of 4-CP resulting from previous spikings (and subsequent anaerobic dechlorination) of 2,4,6-TCP. A mass balance for the same experiment is given in Table 1. The total number of aromatic molecules in the system remained approximately constant, indicating the a mass balance for 2,4,6-TCP and its dechlorination products could be closed. No other reaction products beside those shown in Figure 2 were produced in significant amounts during the reductive dechlorination reaction. These experiments also indicated that the anaerobic culture

Table 1 - Mass Balance for the Anaerobic Dechlorination of 2,4,6-TCP by Anaerobic Consortium in Serum Bottles

Time (hours)	2,4,6-TCP (μM)	2,4-DCP (μM)	4-CP (μM)	Phenol (μM)	Total (μM)	Total (%)
0	108.7	0.0	196.0	8.4	313.1	100
48	59.3	21.9	226.0	8.7	315.9	101
120	0.0	21.0	285.5	11.9	318.4	102
168	0.0	0.0	309.5	21.1	330.6	106
216	0.0	0.0	315.5	26.6	342.1	109
264	0.0	0.0	319.4	26.8	346.2	111

was unable to further degrade 4-CP at any significant rate. When all the 2,4,6-TCP had been degraded to 4-CP an additional spiking of 2,4,6-TCP was made and the process was started anew.

In the aerobic experiments described below a phosphate buffer was added to the aerobic cultures to control the pH. Therefore, experiments were also conducted in which the anaerobic organisms were exposed to phosphate buffers. However, when a phosphate buffer solution was added to the anaerobic bottles bringing the final concentration of phosphate to 50, 100 and 150 mM, respectively, the dechlorination activity slowed down considerably, and came to a complete halt when the phosphate concentration was the highest. Additional details are published elsewhere [25]. Therefore, no phosphate solutions were added to any of the subsequent anaerobic experiments.

Active dechlorination was obtained with immobilized microorganisms when the recirculated anaerobic reactor was used. Figure 3 shows the results. The entire dechlorination process was completed within two days and nearly stoichiometric amounts of 4-CP were recovered. Table 2 shows that the mass balance for this process could be closed within $\pm 12\%$ at all times.

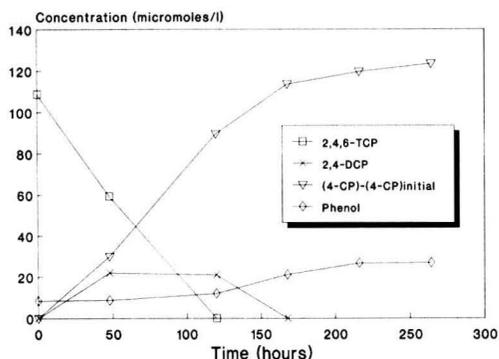


FIGURE 2. Anaerobic dechlorination of 2,4,6-TCP in serum bottles.

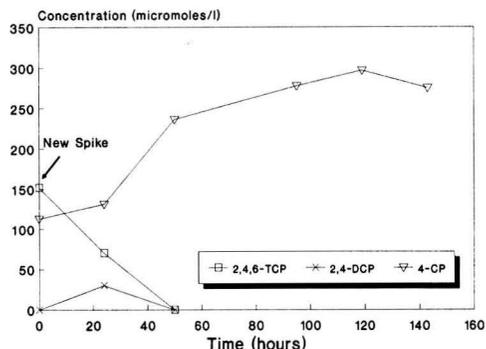


FIGURE 3. Anaerobic dechlorination of 2,4,6-TCP in the recirculated anaerobic reactor.

Table 2 - Mass Balance for the Anaerobic Dechlorination of 2,4,6-TCP in the Recirculation Reactor with Immobilized Microorganisms

Time (hours)	2,4,6-TCP (μM)	2,4-DCP (μM)	4-CP (μM)	Total (μM)	Total (%)
0	152.0	0.0	112.8	264.8	100
24	70.4	30.1	131.4	231.9	88
50	0.0	0.0	236.4	236.4	89
95	0.0	0.0	277.6	277.6	105
119	0.0	0.0	297.0	297.0	112
143	0.0	0.0	275.3	275.3	104

Finally, the anaerobic dechlorination process was tested during and after the immobilization of the microorganisms on R-635 Manville Celite silica beads in the anaerobic reactor of the anaerobic-aerobic system. Dechlorination during the microbial immobilization process was tested by adding a suspension of microorganisms spiked with 101.3 μM of 2,4,6-TCP to the reactor containing the beads. The first sample was taken after 51 hours and showed no trace of 2,4,6-TCP, but only 23.9 μM of 2,4-DCP and 80.1 μM of 4-CP. After one week a biofilm of microorganisms could be observed on the surface of the beads. After 316 hours only 120.5 μM of 4-CP could be found in solution. The system was then spiked with additional 40.5 μM of 2,4,6-TCP which were degraded to 4-CP within one day. Figure 4a summarizes these results. The mass balance for this process is shown in Table 3. To ensure that the immobilized microorganisms were responsible for the dechlorination reaction the content of the reactor was drained and replaced with fresh autoclaved medium spiked with 152 μM of 2,4,6-TCP. The results shown in Figure 4b indicate that 2,4,6-TCP was degraded to 2,4-DCP and subsequently to 4-CP, as previously observed. The mass balance for all

Table 3 - Mass balance for the anaerobic dechlorination of 2,4,6-TCP during the immobilization of the microorganisms on Manville R-635 beads in the anaerobic batch reactor

Time (hours)	2,4,6-TCP (μM)	2,4-DCP (μM)	4-CP (μM)	Total (μM)	Total (%)
0	101.3	0.0	0.0	101.3	100
51	0.0	23.9	80.1	104.0	103
316	0.0	0.0	120.5	120.5	119
*317	40.5	0.0	118.2	158.7	100
336	0.0	0.0	136.1	136.1	86
362	0.0	0.0	141.5	141.5	89
407	0.0	0.0	152.4	152.4	86
431	0.0	0.0	146.2	146.2	92

*New spike

the aromatic compounds in the system was satisfactorily closed, as shown in Table 4. From these experiments it was concluded that the immobilized bacteria were responsible for the dehalogenation reaction.

Aerobic Mineralization of the Anaerobic Dechlorination Products

Results are reported here for two types of cultures, namely *Pseudomonas Glathei* (ATCC culture # 29195) and the indigenous aerobic culture from the anaerobic reactor. *Pseudomonas Glathei* was grown for three days in a shaker flask with the medium obtained from the sterilized supernatant from the treatment plant. Then, 4-CP was added so that its concentration was 140 μM . After 78 hours only 84 μM were left. The culture was spiked again with 4-CP

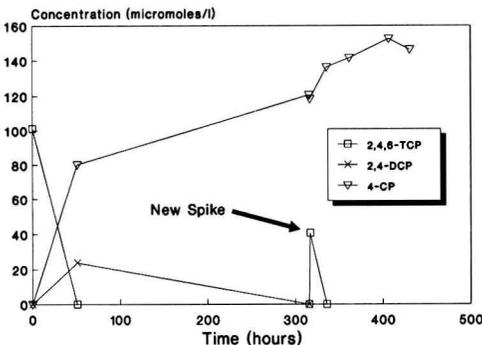


FIGURE 4a. Anaerobic dechlorination of 2,4,6-TCP during the immobilization of microorganisms on Manville R-635 beads in the anaerobic batch reactor.

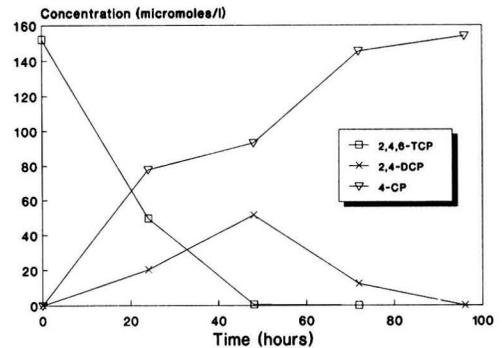


FIGURE 4b. Anaerobic dechlorination of 2,4,6-TCP after the immobilization of microorganisms on Manville R-635 beads in the anaerobic batch reactor.

Table 4 - Mass balance for the anaerobic dechlorination of 2,4,6-TCP in the anaerobic batch reactor after the immobilization phase in the presence of fresh medium

Time (hours)	2,4,6-TCP (μM)	2,4-DCP (μM)	4-CP (μM)	Total (μM)	Total (%)
0	152.0	0.0	0.0	152.0	100
24	49.6	20.2	77.8	147.6	97
48	0.5	51.5	93.3	145.3	96
72	0.0	12.3	145.4	157.7	104
96	0.0	0.0	154.0	154.0	101

(201.4 μM). However, the degradation reaction proceeded at an even slower pace and after 46 hours 168.7 μM of 4-CP still remained in the culture. The experiment was repeated starting with a 4-CP concentration of 165 μM . After 42 hours the pH of the system had risen to about 9 and minimal degradation had taken place (final 4-CP concentration: 147 μM). The culture was reinoculated, and a phosphate buffer was added to lower the pH to the range 7.8 - 8.2. After additional 45 hours the culture was tested for the presence of 4-CP, but no 4-CP was found. When phosphate was not added an increase in pH was also noticed in all the unbuffered aerobic cultures examined. However, no satisfactory explanation for the observed pH change can be provided at the moment.

All successive aerobic experiments were conducted in the presence of different concentrations of phosphate buffer. This markedly increase the degradation effectiveness, as shown in Figure 5. The initial pH's of the *Pseudomonas Glathei* cultures were always between 7.0 and 7.2. Despite the phosphate addition, the pH went up to the final values of 8.41, 7.64, and 7.43 when the phos-

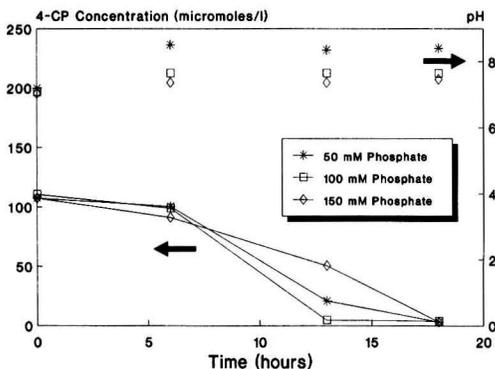


FIGURE 5. Aerobic mineralization of the 4-CP contained in the effluent of the anaerobic batch reactor by *Pseudomonas Glathei* (ATCC # 29195) as a function of phosphate concentration.

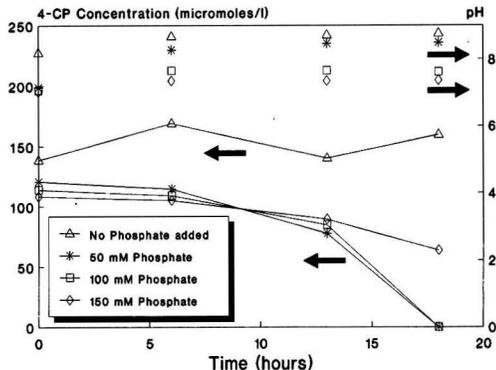


FIGURE 6. Aerobic mineralization of the 4-CP contained in the effluent of the anaerobic batch reactor by the indigenous aerobic culture as a function of phosphate concentration.

phate concentrations were 50, 100 and 150 mM, respectively.

Experiments were also conducted to determine if the anaerobic culture responsible for the 2,4,6-TCP dechlorination also contained aerobic organisms capable of degrading the final dechlorination product, that is, 4-CP. In these experiments the solution from the anaerobic reactor of the anaerobic-aerobic system was drained and transferred to a number of shaker flasks. This solution contained 138.4 μM 4-CP produced from the anaerobic dechlorination of 2,4,6-TCP. No external inoculum was added. Different amounts of phosphate buffer solutions were added to some of the bottles to make the phosphate concentration equal to 50, 100 and 150 mM, respectively. The results are shown in Figure 6. The culture containing no buffer showed no degradation of 4-CP and no change in pH, which remain at a rather high value around 8.7. In the 50 and 100 mM phosphate solutions, the indigenous cultures degraded 4-CP in a period of 18 hours. For an even higher concentration of phosphate, that is, 150 mM, the activity of the culture was inhibited, and the degradation was slowed down appreciably. In all cases, a rise in pH was observed.

These experiments indicate that the aerobic organisms responsible for the degradation of 4-CP were originally present in the anaerobic culture. It was somewhat surprising that aerobic microorganisms could survive in the anaerobic system. However, a similar observation was made before by other researchers, such as McCarty et al. [26], (1962) Toerien [27], (1967) Taylor et al. [28], (1970) Ferry and Wolfe [29], (1976) and Hakulinen et al. [30], (1985) who have isolated *pseudomonas* species from anaerobic conditions. Hakulinen et al. [30] (1985) found that the survival of *pseudomonas* under anaerobic conditions might be due to the presence of another anaerobic microorganism, *Klebsiella oxytoca*.

Results Obtained for the Integrated Anaerobic-Aerobic Process

Batch System

The first experiment conducted in this system utilized the immobilized anaerobic microorganisms that had been used in the anaerobic experiments described above. Prior to this experiment, the anaerobic reactor had not been in use for approximately a month during which the immobilized microorganisms had not been fed any 2,4,6-TCP, but had just been immersed in the sterile medium containing some 4-CP from previous runs. The new experiment began by draining the liquid content of the reactor and replacing it with fresh sterile medium containing resazurin and 106.4 μM of 2,4,6-TCP. The 2,4,6-TCP was not attacked for two days, but it was completely dechlorinated in the following three days, as shown in Figure 7. As the dechlorination reaction began, 2,4-DCP was produced and then converted to 4-CP in another three days. At the end of this period, the concentration of 4-CP reached 104.2 μM , before slightly dropping to 98 μM during the next day. The lag phase in the dechlorination of 2,4,6-TCP was probably due the period of inactivity of the culture during the preceding month. The pH value of the solution started at 8.6 and remained at this level when the 2,4,6-TCP was not dechlorinated. However, at the end of the second day, the pH began to drop from 8.5 to 8.3 in a period of four days. At the beginning of the seventh day, the anaerobic medium was transferred to the aerobic reactor to degrade the 4-CP generated anaerobically. In the aerobic reactor, the initial concentration of 4-CP was 75.1 μM , which was different from the final concentration of 4-CP in the anaerobic reactor (98 μM) because of the addition of the phosphate buffer solution. 4-CP was completely degraded in less than three days. The corresponding pH value increased from 7.2 to 8.0 and then remained constant.

The fast recovery of the anaerobic dechlorination activity against 2,4,6-TCP indicated that the consortium was very stable and that it needed little maintenance to retain its activity. This is consistent with the claim made by Anderson et al. [31] The pH varied in both the anaerobic and aerobic reactors in a manner similar to previous experiments (that is, the pH dropped during the anaerobic reaction and rose in the aerobic one). Volatile fatty acids produced from the sterile sewage under anaerobic processes, and HCl produced from the reductive dechlorination of 2,4,6-TCP, were expected to lower the pH [32].

The entire 2,4,6-TCP degradation process took nine days to complete. However, if the two-day lag period is deducted, and if the anaerobic solution had been transferred just after the complete disappearance of the 2,4,6-TCP from the anaerobic reactor, then the entire process would have been expected to take only six days, roughly evenly divided between the anaerobic and aerobic processes. If the lag period is not accounted for, the dechlorination

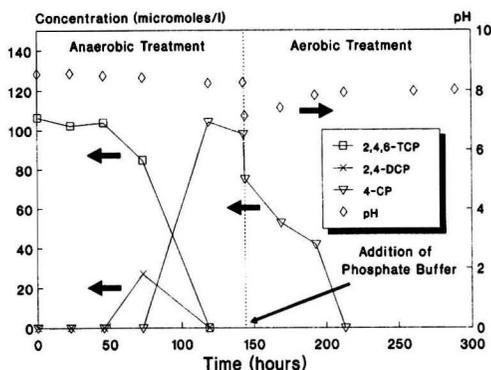


FIGURE 7. Anaerobic-aerobic mineralization of 2,4,6-TCP and pH evolution during batch mode operation.

and mineralization rates are comparable to those obtained in previous experiments (Figures 2 and 6).

A separate experiment was conducted to ensure that the disappearance of 4-CP in the aerobic reactor was not caused by air stripping. The aerobic reactor was charged with the sterilized medium containing 4-CP but no inoculum, and the reactor was sparged with air at the same flow rate used when the microorganisms were present. Over a period of four days the concentration of 4-CP in the reactor dropped by less than 5%.

Continuous System

The anaerobic reactor was first started in the batch mode by spiking it with 231.9 μM of 2,4,6-TCP, all of which disappeared within three days (Figure 8a). Within a period of six days, 2,4-DCP was produced and consumed, and 4-CP accumulated from an initial value of 51.3 μM to 289.3 μM . Meanwhile, 205.3 μM 4-CP had been added to the aerobic reactor containing the indigenous culture. As shown in Figure 8b, 4-CP was mineralized within two days. After 6 days of batch operation (corresponding to the time required for the completion of the slower, anaerobic step) the continuous operation mode began by connecting both reactors as shown in Figure 1b. The system was operated continuously and successfully for the next three weeks. During this period, the feed stream concentration of 2,4,6-TCP was kept approximately constant within the range 113.4 to 130.6 μM . This variation was caused by the extensive length of the experiment and the need to switch feed tanks having slightly different 2,4,6-TCP concentrations.

Figure 8a shows the concentration of the different chlorophenols in the outlet from the anaerobic reactor. The transient operation of the anaerobic reactor before steady state was reached lasted about nine days. This is approximately twice the hydraulic retention time of the anaerobic reactor. The figure also shows that no 2,4,6-TCP was pre-

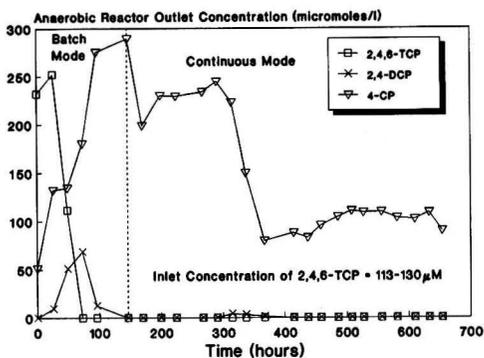


FIGURE 8a. Anaerobic dechlorination of 2,4,6-TCP followed by aerobic mineralization of the dechlorination products.

sent in the outlet from the anaerobic reactor at any time during the continuous operation, and that small concentrations of 2,4-DCP were only present during the transient operation. At steady state the outlet of anaerobic reactor contained 4-CP in nearly stoichiometric amounts with respect to the 2,4,6-TCP fed to the system. Figure 8b shows the corresponding 4-CP concentration at the outlet of the aerobic reactor. 4-CP was completely mineralized throughout the entire continuous operation of the system.

Conclusions

The anaerobic-aerobic process proposed in this work relies on the specific degradation capabilities of two classes of microorganisms to completely degrade toxic halogenated compounds, that is the reductive dehalogenation of highly halogenated molecules of anaerobes, com-

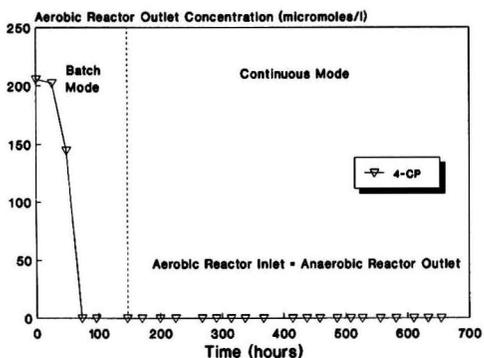


FIGURE 8b. Anaerobic dechlorination of 2,4,6-TCP during the continuous operation of the anaerobic-aerobic process.

bined with the oxidative mineralization of the resulting dehalogenation products by the aerobes. These capabilities appear to be complementary. Therefore, this process is expected to have a potential in the industrial treatment of recalcitrant halogenated aromatic compounds.

Acknowledgments

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Treatment and Stabilization of a Hexavalent Chromium Containing Waste Material

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In order to stabilize such wastes, it is necessary to convert the Cr^{+6} to the trivalent (Cr^{+3}) form, before solidifying the waste through the use of cementitious materials such as portland cement or pozzolime (cement kiln dust). A treatment scheme was developed using ferrous ammonium sulfate (FAS) as reducing agent. With FAS the reaction kinetics are sufficiently rapid at neutral or alkaline pH ranges. With most other reducing agents, such as sodium metabisulfite or ferrous sulfate, it would first be necessary to adjust the pH to about 2 S.U. in order for the reduction reaction to proceed in reasonable time. Bench scale tests were conducted in which the waste material containing about 6,000 mg/kg of Cr^{+6} and with pH approximately 11 S.U., was reacted with varying doses of FAS at pH levels of 4.5, 7, and as received. The reaction was found to be essentially complete after 3 days and selective for Cr^{+6} . Further tests were conducted in which pozzolime was added to the mixture after the reduction. With an approximately 1:1 ratio of FAS: waste and pozzolime ratios of between 0.5:1 and 1:1, residual hexavalent chromium and total chromium concentrations were well below 100 mg/kg of waste, which corresponds to the EP Toxicity limit of 5 mg/L. The costs for full-scale FAS/pozzolime stabilization were estimated. Testing of alternative reducing agents, which would require first acidifying with sulfuric acid, was deemed not warranted. The acid quantities required would be costly, and such operations in field conditions were felt to be not prudent.

Introduction

The use of chromium as an industrial material dates back to the first attempts to produce corrosion resistant metals and coatings over 100 years ago. The discoveries that the addition of chromium to steel in combination with other elements could extend the service life of the metal and that a coating of chromium could be attractive as well as functional set the stage for the use of large quantities of this metal in many products. The concurrent discovery that a number of useful dyes and pigments could be produced from chromium containing compounds further increased the usage of this metal.

The production of chromium and chromium compounds

involves the extraction of this metal from ores and its subsequent purification for use in the various products. Waste materials are generated during the production of chromium metal and ferroalloys, in the production and use of chromate solutions for electroplating and other manufacturing, and in the production of chromium containing pigments and dyes such as chrome oxide green. A number of these waste materials have been designated as hazardous wastes due to their toxicity and leaching potential. See Table 1.

Of the various forms that chromium can exist in, the most toxic is the hexavalent (+6) form. This form, which is commonly found in the raw material for electroplating and occurs as a by-product in the waste materials from most of the other uses of chromium, is very mobile in the environ-

TABLE 1 - Listed Hazardous Wastes Containing Hexavalent Chromium

Industry	Type
F006 Electroplating	Wastewater Treatment Sludge
F019 Conversion Coating of Aluminum	Wastewater Treatment Sludge
K002 Inorg. Pigments (Chrome Yellow & Orange)	Wastewater Treatment Sludge
K003 Inorg. Pigments (Molybdate Orange)	Wastewater Treatment Sludge
K004 Inorg. Pigments (Zinc Yellow)	Wastewater Treatment Sludge
K005 Inogr. Pigments (Chrome Green)	Wastewater Treatment Sludge
K006 Inorg. Pigments (Chrome Oxide Green)	Wastewater Treatment Sludge
K008 Inorg. Pigments (Chrome Oxide Green)	Oven Residue
K048 Petroleum Refining	DAF Float
K049 Petroleum Refining	Slop Oil Emulsion Solids
K050 Petroleum Refining	Ht. Exch. Cleaning Sludge
K051 Petroleum Refining	API Separator Sludge
K061 Iron & Steel	Emission Control Dust/Sludge
K062 Iron & Steel	Spent Pickle Liquor
K065 Primary Lead	Pond Solids
K066 Primary Zinc	Wastewater Treatment Sludge
K069 Secondary Lead	Emission Control Dust/Sludge
K086 Ink Foundation	Miscellaneous
K090 Ferroalloys (Ferrochromium silicon)	Emission Control Dust/Sludge
K091 Ferroalloys (Ferrochromium)	Emission Control Dust/Sludge

Reference: 40CFR 261, Appendix VII

ment and is both an acute and chronic hazard. Numerous sites in the United States where chromium has been used are currently contaminated with this toxic, hexavalent form.

A number of proprietary methods have been introduced in recent years to stabilize a wide range of waste materials so that they may be successfully landfilled. In the case of waste materials containing hexavalent chromium, these methods have not been successful. Up to the present time no universal method of stabilization for these soils has been found. A recent site cleanup resorted to placing untreated hexavalent chromium containing soil in a secure landfill cell until a suitable method to permanently dispose of the material could be developed [1].

Case Study

Metcalf & Eddy (M&E) was retained by an industrial client to investigate the possible stabilization of hexavalent chromium containing soils discovered during a plant property transfer. The hexavalent chromium concentrations of this waste material averaged about 600 mg/kg but in some soils were greater than 6,000 mg/kg (that is, 0.6% chromium).

A number of commercial waste fixation technologies had been tested on a bench scale basis and all had been found to not adequately fix the hexavalent chromium so that an EP Toxicity or a TCLP extraction would yield a suitable extract, that is, one with less than 5 mg/L of chromium.

In order to stabilize hexavalent chromium containing material it is necessary to first convert the hexavalent chromium (Cr⁺⁶) to a more chemically stable form, the trivalent (Cr⁺³) form. Once the chromium is in this reduced form, it is then possible to solidify and stabilize the waste materials through the use of cementitious materials such as portland cement or pozzolime (cement kiln dust).

The use of a reducing agent to convert hexavalent chromium to the trivalent form is widely practiced in treating industrial wastewaters. Chemicals such as sodium metabisulfite (NaHSO₃), ferrous sulfate (FeSO₄), and ferrous ammonium sulfate [FAS] (FeSO₄(NH₄)₂ (SO₄)₂ • 6H₂O) can be utilized to reduce the hexavalent chromium.

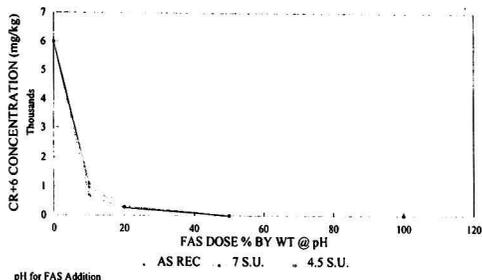


FIGURE 1. FAS treatability testing: leach results after 3 day cure.

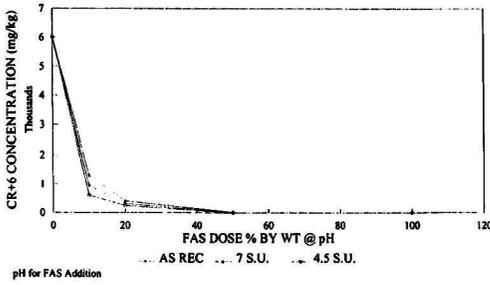
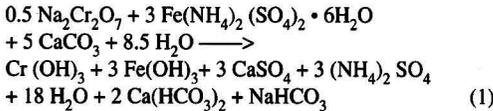


FIGURE 2. FAS treatability test: leach results after 7 day cure.

With most of these reducing agents, it is first necessary to acidify the waste to a pH of approximately 2 S.U. in order for the kinetics of the reaction to proceed in a reasonable time period. However by the use of ferrous ammonium sulfate the reaction kinetics are sufficiently rapid at neutral or even alkaline pH ranges. The overall reaction stoichiometry for chromium reduction with FAS is represented as follows:



In Reaction (1), CaCO_3 represents alkalinity present in the waste material, which is consumed during the reduction.

Reduction Tests

Because of the possible acceptable reaction rates for ferrous ammonium sulfate under alkaline conditions, it was decided to conduct a series of bench scale tests to verify the applicability of this method for the actual waste material, which had a pH of 11 S.U. A series of experiments was conducted in which the most concentrated waste material containing about 6,000 mg/kg of hexavalent chromium was reacted with varying doses of ferrous ammonium sulfate at

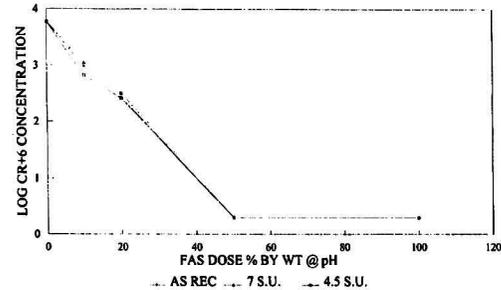


FIGURE 4. FAS treatability: semilog plot of leach results after 3 day cure.

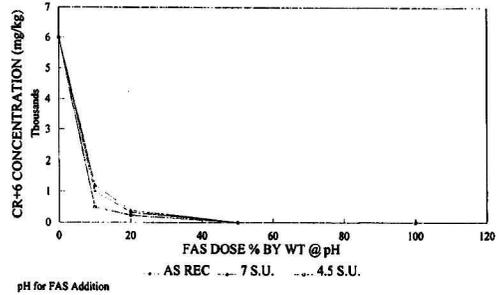
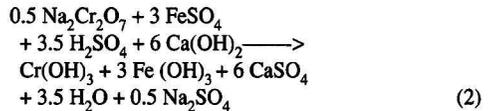


FIGURE 3. FAS treatability test: leach results after 10 day cure.

pH levels of 4.5, 7, and as received (approximately 11). Total chromium and hexavalent chromium were analyzed after 3, 7 and 10 days and the results compared to determine the effects of time or pH levels on the residual hexavalent chromium level. As can be seen in Figures 1 through 3, the reaction was essentially complete after 3 days. It was essentially quantitative until only a low level of hexavalent chromium remained and other side reactions then probably began to be significant. Figure 4 through 6 show the same results on a log basis.

At the same time the alternative use of sodium bisulfite or ferrous sulfate was considered. Although they are capable of producing the required reduction reaction, further testing was deemed not warranted due to the requirement to first reduce the high pH of the waste material to a value of about 2 S.U. and subsequently to neutralize the excess acidity. The overall stoichiometry for the hexavalent chromium reduction, including pre-acidification and post-neutralization reactions is as follows, based on sulfuric acid, ferrous sulfate and lime reactants:



This does not include reactions of the alkalinity of the

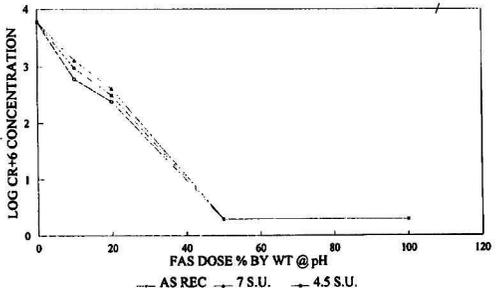


FIGURE 5. FAS treatability: semilog plot of leach results after 7 day cure.

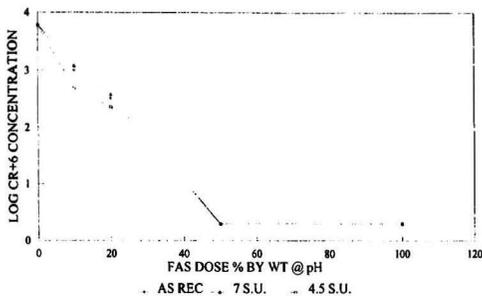


FIGURE 6. FAS treatability: semilog plot of leach results after 10 day cure.

waste material, which averaged about 50,000 mg/kg as CaCO_3 ,



Hence, the acid quantities required would be significant and the use of large quantities of the extremely hazardous material in field conditions was felt to be not prudent as well as costly.

Reduction and Stabilization Tests

Because the ferrous ammonium sulfate successfully reduced the hexavalent chromium to the trivalent form, a further series of tests was conducted in which pozzolime (cement kiln dust) was added to the mixture after the reduction. Residual hexavalent chromium was measured after reacting the waste materials with FAS and pozzolime at varying pH levels. A modified procedure using water extraction at a neutral pH was used to analyze for hexavalent chromium after stabilization. Results showed that a suitable stabilized waste product could be obtained with the

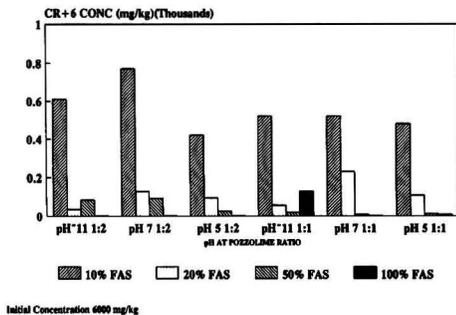


FIGURE 7. FAS - pozzolime leach test results.

addition of approximately a 1:1 ratio of FAS: waste and pozzolime:waste ratios of between 0.5:1 and 1:1. Residual hexavalent chromium and total chromium concentrations were well below 100 mg/kg of the waste, which corresponds to the EP Toxicity limit of 5 mg/L. Figure 7 shows the results graphically.

By-product FAS is available in quantity for an approximate cost of \$200/ton. In the case of a typical waste (600 mg/kg Cr^{+6}) in which this material is mixed at a 10% ratio the cost for in-place disposal (area covered and graded) of the reduced material is approximately \$85/ton. The addition of pozzolime costing \$25/ton at a 0.5:1 ratio will increase this cost to about \$100/ton. The resulting fixed waste is stable and will not leach chromium at TCLP hazardous levels.

Literature Cited

- Hagarty, Edward Patrick, et al., "Chromium - Contaminated Site Remediation for POTW Expansion," *Water Environment and Technology*, 3 (4) (April 1991).

Low Temperature Thermal Treatment for Petroleum Refinery Waste Sludges

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Treatment requirements for waste sludges generated by petroleum refinery operations and designated as waste codes K048, K049, K050, K051 and K052 under the Resource Conservation and Recovery Act (RCRA) became effective in November, 1990 under the "Landban" regulations. An experimental program evaluated low temperature thermal treatment of filter cakes produced from these sludges using laboratory and pilot-scale equipment. One set of experiments on waste samples from two different refineries demonstrated the effective removal of organics of concern from the sludges to meet the RCRA Best Demonstrated Available Technology (BDAT) treatment standards. Cyanides were also within the acceptable limit. Combined with stabilization of heavy metals in the treatment residues, low temperature thermal treatment therefore provides an effective and efficient means of treating refinery sludges, with most hydrocarbons recovered and recycled to the refinery. A milder thermal treatment was used to remove the bulk of the water from a previously filtered waste sludge, providing effective waste minimization through a 40% decrease in the mass of sludge to be disposed. The heating value of the sludge was increased simultaneously by one-third, thereby producing a residue of greater value in an alternative fuels program. A process based on this approach was successfully designed and commercialized.

Introduction

Chemical Waste Management, Inc. (CWM) initiated development of a low temperature thermal treatment process in 1987 after laboratory testing had shown that at the relatively low temperatures of 250-450°C many organic compounds, including high boiling compounds (PCBs), could be successfully separated from solids. Since then, a process termed X*TRAX™ 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 sludges and filter cakes. Economics favor feedstocks with low moisture content, but high moisture feeds, including one that was pumped into the process, have been treated. Organic contaminants can range from high boiling, semivolatile compounds, such as PCBs, polynuclear aro-

matic hydrocarbons and pesticides, to low boiling, volatile compounds such as spent solvents regulated under the Resource Conservation and Recovery Act (RCRA). Mercury is effectively removed, but other metals are left intact.

In the course of the development effort, treatment systems have been built at three distinct sizes, termed laboratory scale, pilot-scale and commercial. Two laboratory units are used for performing treatability studies. One unit is operated by CWM subsidiary Chem-Nuclear Systems, Inc. (CNSI) for performing treatability studies on mixed wastes (RCRA and radioactive). The other unit is operated by CWM's Engineering and Technology Department located in Geneva, Illinois. This unit typically processes one to two kg/hr of waste and is used for tests on RCRA and TSCA (Toxic Substances Control Act) materials. The pilot-scale system, which has a capacity of approximately 4.5

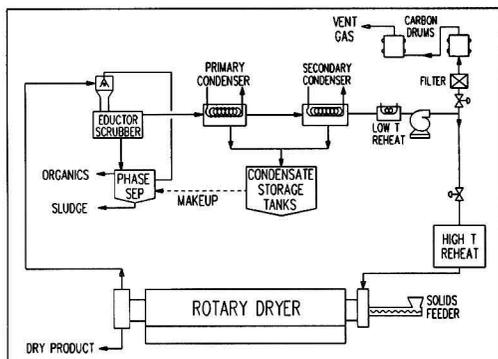


FIGURE 1. Process flow diagram - low temperature thermal treatment process.

metric tons per day, was used to confirm the design parameters and is now used as a demonstration unit. The first commercial unit has been completed and will be moved to a Superfund site in 1992.

Process Description

The process, shown in Figure 1, uses an indirectly heated rotary dryer to volatilize water and organic contaminants in a sealed system. The hot treated solids are cooled and wetted to reduce dust formation using the condensed water removed from the feed. An inert carrier gas (nitrogen) transports the volatilized components to a gas treatment train. This system removes the entrained particulate solids with a scrubber and then cools the entire gas stream to less than 5°C to condense the volatilized organics. Ninety to ninety-five percent of the carrier gas is reheated to 315°C and recycled to the dryer. The remainder of the carrier gas passes through a two micron filter and a carbon adsorption system before being discharged to the atmosphere. The condensed liquid organic removed from the waste is disposed off-site. The sludge

stream, which carries the same waste codes as the original waste feed, can be filtered, with the filter cake added to the feed to the rotary dryer. Detailed descriptions of the process and the units constructed have been presented in previous papers [1, 2, 3].

Refinery Sludges

Petroleum refineries generate waste sludges at a number of sources. RCRA waste codes K048 through K052 are assigned to these wastes depending on the generation source. Table 1 describes the sources of these wastes and indicates the respective volume generated in the U.S. in 1990. K051, API Separator Sludge, was generated in the largest volume, at 409,000 to 545,000 metric tons. K048, Dissolved Air Flotation Sludge, was next highest at 204,000 to 275,000 metric tons. The other three waste types were generated in minor amounts in comparison.

A thermal treatment process operated at a significantly higher temperature than used in the process described in this paper is being used commercially to treat K048-52 wastes [4]. The use of solvent extraction processes [5, 6, 7] is being explored, as is the use of the Carver-Greenfield Process[®] [8]. Incineration is employed commercially, as well as use as a fuel in a cement kiln [9]. This latter concept will be described later in this paper.

Experimental Program

Treatability studies were carried out on four samples of filter cakes produced from refinery sludges. As shown in Table 2, these studies were on two scales, employing the laboratory scale unit and the pilot plant.

Two types of thermal studies were carried out. The first type had as the goal the achievement of the BDAT (Best Demonstrated Available Technology) requirements, especially for the organic compounds as given in the Code of Federal Regulations (40 CFR 268.41). Maximum allowable total concentrations in the treated product are listed for sev-

Table 1 - Petroleum Refinery Waste Sludges U.S. Market Definition^a

Waste Code	Waste Type	Approximate Volume Generated (1990 Metric TPY in 000's)	
		Volume	Percentage
K048	Dissolved Air Flotation Sludge (DAF)	204 - 275	30%
K049	Slop Oil Emulsion Solids (SOES)	34 - 45	5%
K050	Heat Exchanger Bundle Sludge	21 - 27	3%
K051	API Separator Sludge (API)	409 - 545	60%
K052	Tank Bottoms Lead	14 - 18	2%
Total		682 - 910 ^b	100%

^aSource: Chemical Waste Management

^bWet Metric Tons

Table 2
Low Temperature Thermal Treatment Studies

Sample	Waste Codes	Scale	Type of Thermal Treatment
A	K048, 49, 50	Laboratory	Achieve BDAT
B	K051	Laboratory	Achieve BDAT
C	K048, 49, 50	Pilot	Achieve BDAT
D	K048, 49, 50	Laboratory	Dry Only

eral organic compounds and for cyanide. Most of the volatile and semivolatile organics present must be volatilized from the solids to meet the BDAT requirements. The regulations also set limits on the leachability of two metals, nickel and chromium, in the treated waste. The process does not remove metals, with the exception of mercury, and hence would not be expected to be effective in meeting the heavy metals BDAT requirements. Under this mode of operation, essentially all of the water would be expected to be removed.

The other mode of operation listed in Table 2, "dry only," refers to a very mild thermal treatment aimed at removing only the bulk of the water. The goal of this approach is to increase the heating value of the filter cake, making it a more attractive feedstock for an alternative fuels program. Cement kilns now consume the largest volume of these fuels.

Sample A was processed in the laboratory scale system with the goal of meeting the BDAT requirements. The system, located in Geneva, Illinois, was operated under an Illinois authorization for RCRA treatability studies.

The laboratory unit employs an electrical furnace to heat the rotary kiln in place of the propane-fired system used on the pilot- and full-scale systems. The furnace surrounds the kiln, which is a 10 cm diameter by 122 cm long rotating cylinder. The sample A feed material was a refinery waste filter cake which was moist and sticky, but easily crumbled by hand. The filter cake was placed in a hopper and was augered into the feed end of the kiln. A nitrogen sweep gas was also introduced into the kiln. During operation, the material passing through the kiln was heated to 315-425°C. Treated material exited the kiln and was collected in a product hopper as a dry, powdery solid. Volatilized hydrocarbons and water were transported with the nitrogen sweep gas to the gas treatment system. A small fraction of the feed solids was entrained into this gas stream.

The initial step in the gas treatment process was a spray scrubber which removed virtually all of the particulate material and some of the less volatile hydrocarbons. The remaining gas stream, now saturated with water, then passed through two heat exchangers, the second of which was refrigerated, reducing the gas temperature to about 5°C. This stream was then treated with activated carbon and vented. Note that for the pilot and commercial units, most of this gas stream is recycled to the kiln.

Tables 3 and 4 present the key results of the treatability

Table 3 - Results of Laboratory Scale Treatability Study on Sample A Organic Components and Cyanide

Component	Total Constituent Analysis Concentration (mg/kg)		
	Feed	Treated Product	BDAT for K048-50***
Anthracene	14	BDL(13)	28
Benzene	6.9	1.6	14
Benzo(a)pyrene	6.7	BDL(13)**	12
Bis(2-ethylhexyl)phthalate	BDL(13)**	BDL(13)**	7.3
Chrysene	12	BDL(13)	15
Di-n-butylphthalate	BDL(13)**	BDL(13)**	3.6
Ethylbenzene*	50	0.33	14
Naphthalene*	110	BDL(13)	42
Phenanthrene	30	BDL(13)	34
Phenol	BDL(13)**	BDL(13)**	3.6
Pyrene	16	BDL(13)	36
Toluene*	50	1.7	14
Xylenes*	130	0.84	22
Cyanide	1.2	BDL(0.5)	1.8

*Exceeded BDAT standards in feed.

**BDAT standards are lower than method detection level.

***Nonwastewaters

BDL(X) = Below detection limit of X mg/kg

Table 4 - Results of Laboratory Scale Study for Sample A Heavy Metals

Component	TCLP Leachate Concentration (mg/l)		
	Feed	Treated Product	BDAT for K048-50*
Chromium	< 0.05	< 0.05	1.7
Nickel	< 0.07	< 0.07	0.20

*Non-wastewater. Most stringent requirements for the K048, K049 and K050 waste codes.

study and compare them with the most stringent BDAT treatment standards for the nonwastewater K048, K049 and K050 waste codes. Analyses are shown for the organics and heavy metals for which BDAT treatment requirements are listed. Note that BDL(X) refers to an analytical result being below a detection limit of X mg/kg. Detection limits are variable, depending on the sample matrix and, at times, the size of the sample. For organics, total constituent analysis (TCA) is mandated. Ethylbenzene, naphthalene, toluene and xylenes TCA concentrations clearly exceeded the BDAT requirements in the feed. Unfortunately, the detection levels for three components, bis(2-ethylhexyl)phthalate, di-n-butylphthalate, and phenol, were higher than the treatment standards, though we view this as more of a regulatory issue than a treatability issue. Lower detection lev-

els for these compounds may be possible with specialized analytical procedures. However, the laboratory used for these analyses routinely estimates constituent concentrations at levels down to one tenth of the stated detection level. No estimates were provided, and their absence provides evidence that these materials were not present in the feed at concentrations above the treatment standards.

Using the same arguments, the information presented in the "Treated Product" column in Table 3 provides evidence that the treatment standards were met for all organic components and for cyanides. Note especially the dramatic reductions for ethylbenzene, naphthalene, toluene and xylenes, the four components which clearly exceeded the treatment standards in the feed.

Table 4 shows that both the feed and product samples leached chromium and nickel at well below the treatment standard, as indicated by the regulation-mandated toxicity characteristic leaching procedure (TCLP).

Sample B, carrying waste code K051, was obtained from a different refinery. The laboratory scale treatability study used essentially the same procedure as that used for sample A, with the goal again being the meeting of BDAT standards. Results are shown in Tables 5 and 6. Only anthracene clearly exceeded the BDAT requirements in the feed. Again, estimates are provided for concentrations down to one-tenth of the detection limit. Based on this guideline, evidence is presented that all other organics met the BDAT requirements with the possible exception of di-

Table 5 - Results of Laboratory Scale Treatability Study on Sample B Organic Components

Component	Total Constituent Analysis Concentration (mg/kg)		
	Feed	Treated Product	BDAT for K048-50***
Anthracene*	110	BDL(33)	28
Benzene	BDL(0.2)	BDL(0.095)	14
Benzo(a)anthracene	BDL(74)**	BDL(33)	20
Benzo(a)pyrene	BDL(74)**	BDL(33)	12
Bis(2-ethylhexyl)phthalate	BDL(74)**	BDL(33)	7.3
Chrysene	BDL(74)**	BDL(33)	15
Di-n-butylphthalate	BDL(74)**	BDL(66)	3.6
Ethylbenzene	0.84	BDL(0.095)	14
Naphthalene	38****	BDL(33)	42
Phenanthrene	BDL(74)**	BDL(33)	34
Phenol	BDL(74)**	BDL(33)	3.6
Pyrene	BDL(74)**	BDL(33)	36
Toluene	1.1	0.14	14
Xylenes	7.2	BDL(0.095)	22

*Exceeded BDAT standards in feed.

**BDAT standards are lower than method detection level.

***Non-wastewaters

****Estimate

BDL(X) = Below detection limit of X mg/kg

Table 6 - Results of Laboratory Scale Treatability Study on Sample B Heavy Metals

Component	TCLP Leachate Concentration (mg/l)		
	Feed	Treated Product	BDAT for K051*
Chromium	BDL(0.05)	BDL(0.05)	1.7
Nickel	0.21	BDL(0.07)	0.20

*Non-wastewater.

BDL(X) = below detection limit of X mg/l

n-butylphthalate for which the BDAT standard was less than one-tenth of the detection limit.

As shown in Table 6, chromium was well below the BDAT standard in both the feed and product. Nickel leached at just slightly above the standard in the feed, but was well below the standard in the treated product. Apparently, nickel was converted to a less soluble form during the thermal treatment process.

For pilot-plant testing, sample C was obtained from the same refinery as Sample A, which was used for the initial laboratory scale study. This sample again carried waste codes K048, K049 and K050, and the treatment goal was meeting the BDAT standards. The moisture content was 49% by weight and the oil and grease content was 23%.

For this study, the pilot plant was located at CWM's Kettleman Hills, California facility. As previously stated, the kiln on the pilot plant was propane-fired, and 90 to 95%

of the nitrogen sweep gas was recycled to the kiln. Otherwise, the process and treatment procedure were similar to those of the laboratory unit. A total of 1,050 kg of filter cake was fed to the pilot plant at an average feed rate of 145 kg/hr.

After processing through the pilot plant, the moisture content of the filter cake was nil, and the oil and grease level had been reduced to 3.4%. Table 7 presents the analytical results for organics and cyanide.

The feed sample was a composite, based on three samples from each of several drums of material fed to the process. The treated product analysis was carried out on a single sample collected after reaching a steady-state operating condition.

The pilot plant was operated at three sets of conditions. The primary variables for a kiln are feed rate and temperature. The feed rate for the three runs was kept constant at 145 kg/hr. Kiln set point temperatures were varied over a relatively narrow range, resulting in product temperatures in the 290-360°C range. The data presented in the "Treated Product" column are from the run carried out at the upper end of the temperature range, which gave the best results. Seven organic components of the feed filter cake clearly exceeded the BDAT standards, and these are marked with a single asterisk in the table. Phenol might have exceeded the standard; the detection level was more than ten times the BDAT standard.

Inspection of the "Treated Product" column then reveals the most important findings presented in this paper. Concentrations of all organics of regulatory concern were

Table 7 - Results of Pilot Plant Treatability Study on Sample C Organic Components and Cyanide

Component	Total Constituent Analysis Concentration (mg/kg)		
	Feed	Treated Product	BDAT for K048-50***
Anthracene	9.2	0.37	28
Benzene	BDL(5)	BDL(0.5)	14
Benzo(a)pyrene	BDL(100)**	BDL(2)	12
Bis(2-ethylhexyl)phthalate*	373	BDL(2)	7.3
Chrysene	BDL(100)**	1.3	15
Di-n-butylphthalate*	69	BDL(2)	3.6
Ethylbenzene*	40	BDL(0.5)	14
Naphthalene	19	1.4	42
Phenanthrene*	44	1.9	34
Phenol	BDL(100)**	0.46	3.6
Pyrene*	57	1.3	36
Toluene*	29	8.7	14
Xylene(s)*	203	BDL(0.5)	22
Cyanide	0.5	—	1.8

*Exceeded BDAT standards in feed.

**BDAT standards are lower than method detection level.

***Non-wastewaters

BDL(X) = Below detection limit of X mg/kg

Table 8 - Results of Pilot Plant Treatability Study on Sample C Heavy Metals

Component	TCLP Leachate Concentration (mg/l)		
	Feed	Treated Product	BDAT for K048-50*
Chromium	0.28	2.7, 0.24	1.7
Nickel	0.25	0.55, 0.26	0.20

reduced to well below the BDAT standards. These results were found on a large pilot scale, with a pilot plant which closely simulates the full-scale process.

Cyanides were present in the feed at the 0.5 mg/kg level. They were not analyzed for in the product sample represented in Table 7, but, as would be expected from the 0.5 mg/kg concentration in the feed, they were well below the regulatory requirement of 1.8 mg/kg in samples obtained at the two less optimal pilot plant operating conditions. Actual measurements were 0.9 and 0.2 mg/kg.

Results for metals leaching are shown in Table 8. Again, results are shown for the two less optimal run conditions. The BDAT standards were not achieved, and additional treatment of this waste stream would be required before disposal. The logical choice would be the addition of a metals stabilization step. On the full-scale system, the treated solids discharged from the dryer are conveyed to a blender in which condensed water from the process is used to cool and wet the solids. It would be relatively straightforward to add a reagent silo, a reagent metering system and a waste/reagent ratio control system to carry out the required stabilization.

The condensed oil recovered from the phase separator had an ash content of less than 0.5% and a heating value of 10,800 cal/g (19,400 Btu/lb). Recycling of this stream to the refinery as a slop oil for refining is entirely feasible.

Since treatability studies were carried out on both the laboratory and pilot scale on samples from the same refinery, it is of interest to compare the results obtained on the two scales. By comparing the results shown in Tables 3 and 7, it can be observed that both systems were able to yield treated products with organic component concentrations below their BDAT treatment standards. Overall percentage removal of organics for the two scales was remarkably similar, with 98.9 found for the laboratory unit vs. 98.2 for the pilot plant.

Sample D was obtained from yet a third refinery. As previously stated, this material was processed through the laboratory unit with different objectives from that employed for samples A, B and C. The goal was to remove most of the water, leaving the hydrocarbons and solids intact. One would of course expect that some of the more volatile hydrocarbons would be removed along

with the water, and this is in fact what happened.

The procedure used for treating sample D was essentially the same as that used for samples A and B, with the exception that considerably lower temperatures were employed. The results are shown in Table 9, which shows heating value, oil and grease, solids and water contents for feed and treated product samples. A key result is the increase in heating value from 4,000 cal/g to 5,330 cal/g (7,200 Btu/lb to 9,600 Btu/lb). This substantial (33%) increase in the heating value makes the waste stream a much more viable candidate for an alternative fuels program. The most likely use of this stream would be as fuel to a cement kiln. It would either be added to the kiln as a solid, or, more likely, it would be slurried with a liquid fuel and fed to the kiln in a liquid form.

Assuming conservation of the solid fraction, the data in Table 9 imply that about 97% of the water and 28% of the oil was removed from the feed. The thermal desorption process recovers these materials as condensate. In a refinery, the oil fraction would be recycled, and the water would be sent to a wastewater treatment process. About 60% of the original mass remains, providing a substantial reduction in the amount of waste which is sent off-site.

The data generated for sample D were used to design and successfully commercialize a mobile sludge drying system with a capacity of about three tons per hour. This system is similar in concept to the X*TRAX process and is now in commercial use at oil refineries.

Conclusions

Low temperature thermal treatment is an effective and efficient technique for meeting BDAT standards for RCRA waste codes K048, 49, 50 and 51, sludges from petroleum refinery operations. Effectiveness was demonstrated on a pilot scale at an operating rate of 145 kg/hr.

Low temperature thermal treatment can also be effectively employed to reduce the volume of sludge generated by a refinery, while at the same time increasing by one-third the heating value of the residue, which may then be used in an alternative fuels program. A process based on the laboratory study discussed in this paper has

Table 9 - Results of Laboratory Scale Treatability Study on Sample D

	Feed	Treated Product
Heating Value	4,000 cal/g (7,200 Btu/lb)	5,330 cal/g (9,600 Btu/lb)
Oil and Grease, Wt %	34	30
Solids, Wt %	41	68.4
Water, Wt %	25	1.6

been successfully commercialized.

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Formation of NO_x by Digestion of Phosphate Ores with Concentrated Nitric Acid

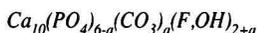
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The digestion of twelve phosphate ores with concentrated nitric acid has been studied in order to quantify the formation of nitrogen oxides, NO_x . The experiments were performed in a batch laboratory-scale reactor under reaction conditions which are representative of the acidulation of phosphate rock with nitric acid in the nitrophosphate process, an important process for the production of compound fertilizers. The results obtained from these experiments show that the amount of NO_x formed during digestion is directly proportional to the organic carbon content and is only marginally related to the carbonate and fluoride contents of these phosphate ores. It is assumed that organic material in the ores is partly oxidized by nitric acid, which in its turn is reduced to NO and NO_2 . On the basis of our results the following correlation between the organic carbon content and the quantity of nitrogen produced in the form of nitrogen oxides is proposed: $[\text{NO}_x\text{-N}] = A \cdot [\text{C}_{\text{org}}]$ in which $A = 0.65$ if $[\text{NO}_x\text{-N}]$ and $[\text{C}_{\text{org}}]$ are both expressed on a weight basis and $A = 46$ if $[\text{NO}_x\text{-N}]$ and $[\text{C}_{\text{org}}]$ are expressed in mol/tonne of P_2O_5 and kg/tonne of P_2O_5 , respectively. The result is important in specifying the value of phosphate ores for the nitrophosphate process because it quantifies the possible emissions of NO_x into the atmosphere as well as the amount of wasted nitric acid.

Introduction

Phosphoric acid is an important chemical intermediate, which is used in many areas of the chemical industry, mainly as an ingredient in the production of fertilizers. Phosphate ore or phosphate rock is the raw material for the production of phosphoric acid. Most phosphate rocks are basically made up of calcium phosphate containing varying quantities of other anions and cations. The most common constituents are fluorapatite, francolite, dahllite and hydroxyapatite. The chemical composition of all these compounds is expressed as:



In acidulation the various phosphates ores exhibit a wide range of chemical reactivities connected to differences in geological origin. Most of the phosphates used for the production of phosphoric acid are sedimentary phosphates, also called marine phosphates, and have been formed by

precipitation of dissolved phosphate from prehistoric seas. These phosphates generally contain a lot of impurities. Phosphates of igneous origin, which for instance are found in northern Europe, generally have a high phosphate content. Ores of sedimentary origin are in general much more reactive and tend to be softer, which means they need less grinding. Moreover, the deposits are usually larger, easier to mine and located closer to the coast than igneous phosphates. Over 50 elements are present in phosphate rock as impurities [1]. Fortunately, however, most of them are present in very low concentrations. The impurities are in general undesirable because they influence production and product quality (for example, aluminium, iron, magnesium and carbonate), are a dangerous pollutant (for example, fluorine), are poisonous (for example, cadmium), cause corrosion (for example, chloride), cause erosion (for example, silicon) or are even radioactive (for example, radium and uranium).

Phosphoric acid production processes fall into two categories: wet processes and furnace processes [1-4]. Furnace

process acid is made through reduction of phosphate ore to phosphorus, which is subsequently oxidized and hydrated. Wet process acid, which is mainly used for fertilizer production, is produced by the reaction of a (mixture of) strong mineral acid(s) with the phosphate rock. To destroy the apatite lattice sulphuric (mostly), phosphoric, nitric or hydrochloric acid is used. For the processes based on this latter technique the calcium to phosphate ratio is important because it determines the amount of acid needed for the production of a certain amount of phosphoric acid. Ores with a high calcium content and a low phosphate value give large quantities of wastes after acidulation (gypsum, if sulphuric acid is used as digestion agent), which can sometimes cause large environmental problems. Nitric acid is widely used, especially in western Europe, in the acidulation of phosphate rock to produce nitrophosphate; the acid is used for dissolution of the ore at moderate temperatures (60 - 85°C) as well as for the addition of nitrate nutrient to the fertilizer product. To obtain a highly water soluble phosphate the calcium has to be partly or completely removed before the acidulate is ammoniated and dried to give a solid nitrophosphate product. Compound fertilizer types, which contain nitrogen, phosphorus and potassium, can be produced via addition of a potassium salt, in general potassium chloride or potassium sulphate, to the mixture before the water is evaporated and the slurry is solidified by granulation or prilling. The calcium can be removed by granulation or prilling. The calcium nitrate crystallizes and can be separated by filtration or centrifuging (Odda process). Another method, used by DSM, is the removal of the calcium as calcium sulphate dihydrate (gypsum) obtained by precipitation of the calcium with ammonium sulphate. In Figure 1 a schematic representation of the DSM gypsum precipitation nitrophosphate process is given. In the first step of the nitrophosphate process, the digestion of the phosphate rock with concentrated nitric acid, side-reactions occur due to the presence of impurities in the raw material [5,6]. During the acidulation, for instance, fluorine is partly liberated as hydrogen fluoride, carbonate is decomposed to carbon dioxide and organic material is partly oxidized. Due to this oxidation nitrate ions are reduced to nitrogen oxide, NO, and nitrogen dioxide, NO₂, giving rise to NO_x emission. The combination of production of gaseous components (mainly carbon dioxide) and the presence of organic material may lead to formation of stable foams which cause problems in the digestion section of the nitrophosphate plant. High concentrations of organic material may also lead to problems in the filtration section of the calcium containing by-product and to discoloring of the final fertilizer granules. The emissions of hydrogen fluoride and nitrogen oxides can be reduced by efficient scrubber systems. The work reported in this paper concerns the formation of NO_x by digestion of phosphate rocks with concentrated nitric acid. Based on the experimental data on 12 rocks from different origin it is shown that there is a correlation between the content of organic

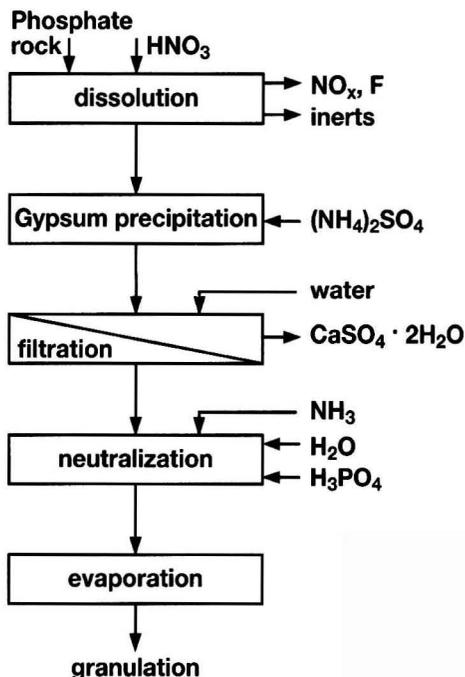


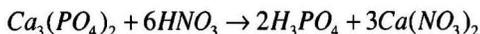
FIGURE 1. Schematic representation of the DSM gypsum precipitation nitrophosphate process for the production of NP(K) fertilizers.

material in these ores and the quantity of nitrogen oxides produced.

Chemistry

Due to the complex nature of phosphate rock, the digestion involves several reactions. For the sake of simplicity the overall dissolving reaction with nitric acid is subdivided into the reactions with the three major calcium salts.

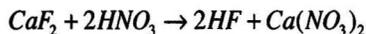
A. Tricalcium phosphate is converted to phosphoric acid and calcium nitrate:



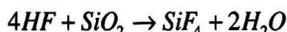
B. Calcium carbonate reacts with nitric acid to produce carbon dioxide, calcium nitrate and water:



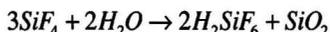
C. Calcium fluoride is converted to hydrogen fluoride and calcium nitrate:



The hydrogen fluoride formed may react with silica to produce silicon tetrafluoride:

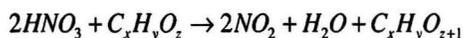


The silicon tetrafluoride may hydrolyze to fluosilicic acid:

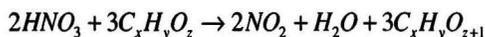


In industrial practice the quantity of nitric acid used for the dissolution of phosphate ore depends on the process that has been chosen and is between 5 percent deficiency up to an excess quantity of 25 percent with respect to the stoichiometry.

Nitric acid is a powerful oxidizing agent; it reacts with reducing agents via several routes. The two main redox reactions between nitric acid and organic matter can be represented as:



and



where nitrogen peroxide and nitrogen oxide are produced, respectively. These reactions have been the subject of the investigation.

Experimental

Figure 2 shows the experimental set-up used to determine the production of nitrogen oxides in the digestion of phosphate rocks with concentrated nitric acid. The digestion reactor (1), which is a glass cylindrical flat-bottom vessel with a volume of 1.0 dm³, is equipped with a two-bladed stirrer (2), a temperature sensor (3), a phosphate ore inlet (4), a gas inlet for air (5) and a gas outlet (6). The temperature of the reaction mixture is kept constant by a thermostatted jacket (7). The digestion starts after a weighed amount of phosphate rock is added to a precalculated quantity of concentrated nitric acid. The initial temperature of the nitric acid is about 20°C lower than the final reaction temperature. Simultaneously, with the beginning of dosing of phosphate ore, a fixed flow of air is introduced into the reactor (via (5)). With this air stream nitrogen oxides formed during digestion are led via a cooler (8) to an NO_x-absorber (9). This absorber is a packed column

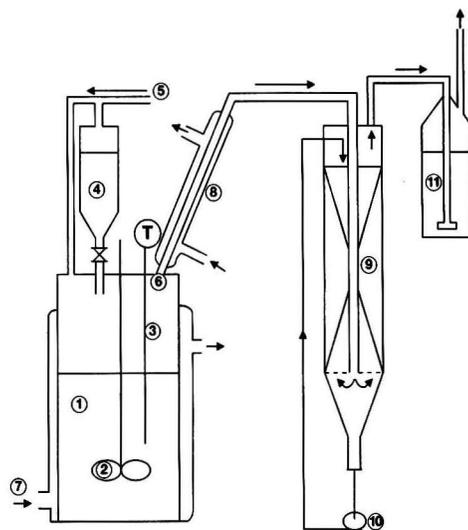


FIGURE 2. Experimental setup used to determine the quantity of NO_x formed by digestion of phosphate ores with nitric acid. 1. digestion reactor, 2. two-bladed stirrer, 3. temperature sensor, 4. phosphate ore inlet, 5. gas inlet for compressed air, 6. gas outlet, 7. thermostatted water bath, 8. gas cooler, 9. packed column NO_x-absorber, 10. liquid circulation pump, 11. 'police' bubble column NO_x-gas absorber.

which is operated countercurrently (liquid flows downwards and gas upwards). The column is filled with Berl-saddles to obtain a large gas-liquid contact area. The absorption liquid is an aqueous 2 molar sodium hydroxide solution with approximately 3 wt % hydrogen peroxide and is circulated during the digestion (10). In this column the oxides of nitrogen are quantitatively absorbed and converted to nitric acid. Finally, the scrubbed gas stream is fed to a semi-batch wise operated bubble column (11), with a sintered gas distributor to produce small gas bubbles. This column, which is also filled with the aqueous 2 N NaOH solution with 3 wt % H₂O₂, acts as a 'police absorber', catching small quantities of non-absorbed NO_x from the gas stream. The experiment is continued for 30 minutes after the dosing of phosphate ores is stopped. Then the total amount of nitrogen in the liquid in the packed column absorber as well as in the bubble column absorber is determined (Kjeldahl method; Vapodest; error: approx. 3%) and the NO_x-emission, expressed as kg NO_x-N / tonne P, is calculated. More experimental details are given in Table 1. The experimental work was performed with 12 samples of phosphate rocks. In a few cases different samples from the same producer were used. Due to the natural origin of the raw material even in these cases the composition was not constant. The chemical composition of the ores used in this

Table 1 - Operating conditions

Quantity of phosphate rock	0.250 kg
Quantity of nitric acid	a = 0.15#
Concentration of nitric acid	56 - 60 wt %
Reaction temperature	75°C
Pressure	almost atmospheric
Air flow	3 10 ⁻³ m ³ .s ⁻¹
Reaction time after phosphate dosing is stopped	30 min.
Volume of digestion reactor	1.0 10 ⁻³ m ³
Volume of packed column	1.2 10 ⁻³ m ³
Volume of bubble column	0.3 10 ⁻³ m ³

a is defined as the molar excess of HNO₃ compared to CaO per mole P₂O₅ after digestion, so a = (HNO₃ - 2CaO)/P₂O₅ (mol. ratio).

study is shown in Table 2.

To determine the organic carbon content of the phosphate rock a sample was weighed and acidified with sulphuric acid to remove carbonate. The resulting product was heated to 900°C and the CO₂ now formed was measured by

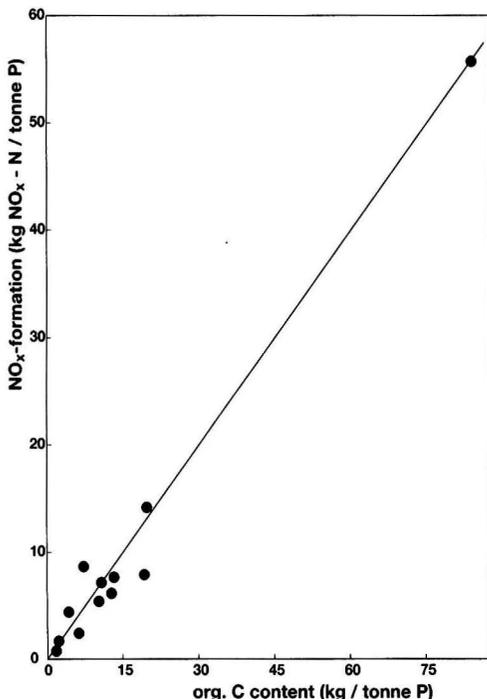


FIGURE 3. The amount of NO_x formed by digestion of phosphate ores with concentrated nitric acid against the organic carbon content of these ores.

infrared spectroscopy. The error is approx. 5%. It is common practice to express the grade of phosphate rock either as P, P₂O₅, or by its BPL (= Bone Phosphate of Lime) content, which is the phosphate content measured as tricalcium phosphate, Ca₃(PO₄)₂.

Results and Discussion

All experiments were performed with a fixed quantity of phosphate rock and a fixed excess of nitric acid in relation to the phosphate content. The applied excess of nitric acid, given in Table 1, is in reasonable agreement with conditions applied in nitrophosphate plants. The experimentally determined amounts of nitrogen oxides formed during the digestion of the several phosphate rock samples are given in Table 2. Figure 3 shows the relation between the organic carbon content of these ores and the measured quantities of oxides of nitrogen formed. It is clear from this figure that the amounts of NO_x produced during the acidulation with concentrated nitric acid are directly proportional to the organic carbon content of the used rocks. As a check for a possible correlation between the carbonate or fluoride content of these rocks and the NO_x emissions, Figures 4 and 5 show the effects of the CO₂ and the fluoride contents on the amounts of oxides of nitrogen formed during digestion, respectively. From these two figures it can be seen that the produced amounts of NO_x are only marginally dependent on the carbonate and fluoride concentrations.

On the basis of these results the following correlation between nitrogen in the form of oxides, NO_x-N, and organic carbon, C_{org}, is proposed:

$$(\text{NO}_x\text{-N}) = A \cdot (\text{C}_{\text{org}}) \quad (1)$$

in which A = 0.65 if [NO_x-N] and [C_{org}] are both expressed on a weight basis, A = 0.56 if [NO_x-N] and [C_{org}] are both expressed on a mole basis and A = 46 if [NO_x-N] and [C_{org}] are expressed in mol/tonne of P₂O₅ and kg/tonne of P₂O₅, respectively. The numerical constants were obtained by the least-squares method. The value of the correlation coefficient is 0.99. With the aid of the simple formula (1) and knowledge of the organic carbon content of a phosphate ore, the maximum NO_x emission can be easily predicted. If we assume that the organic carbon in the rock is present in the form of - (CH₂)_n - and is completely oxidized to carbon dioxide and water and that the nitric acid is reduced in equal amounts to NO and NO₂ then four moles of NO_x should be formed per mole of organic carbon. This value is much larger than the experimentally determined value of 0.56 mol NO_x/mol C_{org}, which means the organic components are only partially oxidized.

In contrast to other wet phosphoric acid processes, in the nitric phosphate process there is the environmental problem of controlling emissions of oxides of nitrogen formed by partial reduction of nitric acid by organic materials. In addition, more nitric acid per tonne of final product

Table 2 - Composition and NO_x-Production During Dissolving in Nitric Acid of the Phosphate Rocks Used in this Study

	phosphate			CaO	CO ₂	F	SiO ₂	H ₂ O	CaO/P ₂ O ₅	ignition		organic c	NO _x -production
	P	P ₂ O ₅	BPL							Losses			
	%	%	%	%	%	%	%	%	mol/mol	%	%	kg/tonne P	kg NO _x -N/tonne P
Bucraa	15.5	35.45	77.5	50.75	2.0	4.0	5.4	1.35	3.62	2.3	0.07	4.5	4.3
Djebel Onk	14.2	32.5	71.0	53.50	2.0	4.0	1.8	0.10	4.17	2.1	0.09	6.3	2.4
Florida	14.6	33.45	73.1	47.65	3.1	3.5	4.5	1.5	3.61	10	0.28	19.2	14.5
Jordan-1	14.4	33.05	72.2	50.15	4.5	3.5	4.5	1.1	3.84	7	0.14	9.7	5.5
Jordan-2	14.7	33.6	73.4	51.75	4.7	3.5	2.0	0.37	3.90	5	0.18	12.3	6.4
Khouribga-1	13.9	31.75	69.4	50.80	5.2	3.8	1.3	1.35	4.05	7.4	0.18	13.0	7.8
Khouribga-2	14.1	32.30	70.6	50.90	4.7	3.2	2.0	1.0	3.99	6	0.15	10.6	7.2
Khouribga-3	13.2	30.3	66.2	49.6	5.8	3.5	3.9	1.0	4.14	8	0.25	18.9	8.2
Kola	16.7	38.2	83.5	51.3	0.1	2.1	2.2	1.15	3.40	N.A.	0.035	2.1	1.4
Palfos	17.3	39.55	86.4	53.85	1.2	2.5	0.2	N.A.	3.45	1.2	0.03	1.7	1.2
Sraouertane	13.0	29.7	64.9	49.2	7.3	2.6	4.4	0.3	4.19	8.5	1.1	84.9	55.7
Zinn	14.9	34.1	74.5	54.50	3.5	3.0	0.3	0.1	4.05	N.A.	0.11	7.4	8.6

N.A. = not analyzed

is used because some of the nitric acid is reduced, which increases the production costs of the fertilizers. The envi-

ronmental problem has been approached from two different angles: reducing the emission of the pollutants by eliminating the sources or removing the pollutants before they leave the plant with the off-gases.

Reduction of the formation of NO_x can be done by applying phosphate rocks with a low organic carbon content. To reduce the content of organic material, which is present in all marine phosphates, the raw phosphate rock can for instance be calcined at a high temperature to drive off the organic material prior to usage in the nitrophosphate plant. As already shown, the organic impurity content of phosphate rocks varies widely. In some cases the calcination process can even be performed autothermally, that is, without additional fuel. In general, calcining is an expensive process step. It is performed on a large scale by only a few raw material producers, and of course it has an impact on the cost price of the ores from these producers. Reduction of the amount of desorbed NO_x-gas from the digestion vessels to the off-gas stream can be achieved by adding chemicals to the reaction mixture. Addition of for example, a few kilograms of urea (CO(NH₂)₂) per ton of phosphate rock already reduces the NO_x-emission significantly. If the final product contains unreacted urea, its quality (for example, caking tendency) will deteriorate. Therefore it is not recommendable to add excessive quantities of urea, even through this will result in further reduction of NO_x-emission. Urea reacts with the oxides of nitrogen in the liquid phase before they are desorbed to the gas phase and reduces them to inert nitrogen.

Finally, the off-gas stream can be scrubbed with water for the partial removal of NO_x. A simple and effective way is using a scrubber of the open spray tower type in combination with a collecting device for fine droplets. The last two options increase both the fixed costs, due to invest-

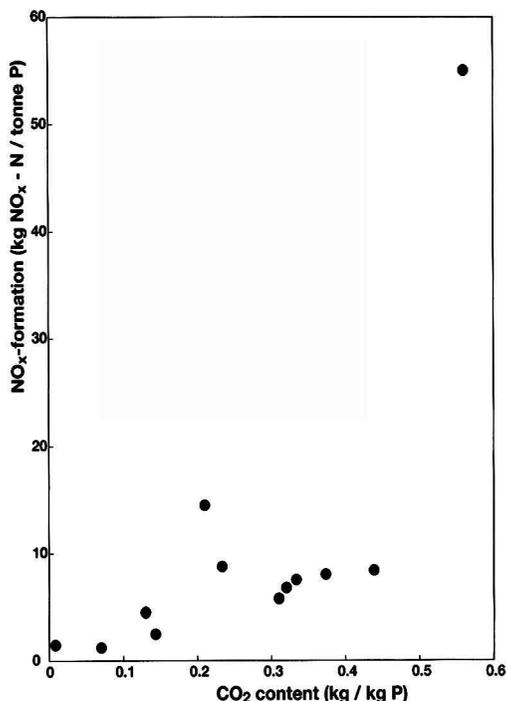


FIGURE 4. The quantity of NO_x formed by acidulation with nitric acid against the CO₂ content of the phosphate ores.

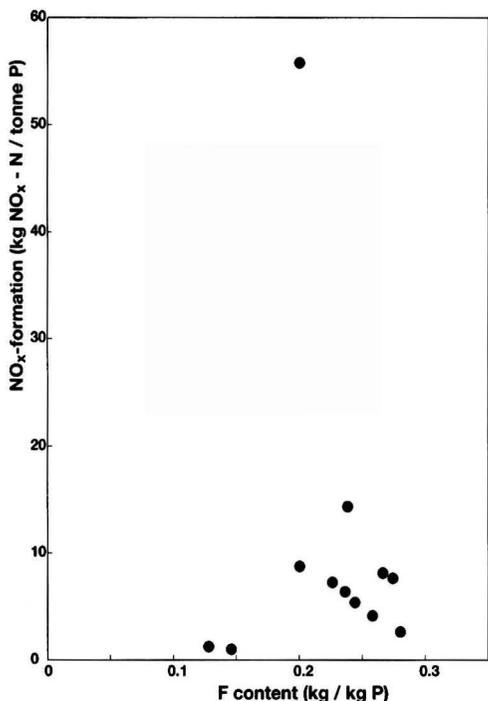


FIGURE 5. The quantity of NO_x formed by acidulation with nitric acid against the fluoride content of the phosphate ores.

ments, and the variable costs due to usage of chemicals and effluent treatment. In practice a combination of the above-mentioned environmental control measures is applied to reduce the emission of oxides of nitrogen to within the specified limits.

Conclusion

From the experimental results obtained during this investigation, it is clear that the quantities of nitrogen oxides formed by digestion of phosphate rocks with concentrated nitric acid are directly proportional to the organic carbon content of these ores. Furthermore it is seen from the present work that these amounts of NO_x are not directly related to the carbonate and fluoride concentrations of the

various phosphate ores used. It was found that approximately 0.65 kg of NO_x-N (= 46 mol NO_x) was formed per kg of organic carbon in these raw materials.

Acknowledgement

The author thanks DSM Agro for their kind permission to publish this study. He also thanks Mr. J.W.M. Deumens for performing the experiments.

Nomenclature

a	=	constant
A	=	constant (Eq. 1)
BPL	=	phosphate content measured as Ca ₃ (PO ₄) ₂
CaO	=	calcium content measured as CaO
CO ₂	=	inorganically bound carbon (e.g. CO ₃ ²⁻) content
C _{org}	=	organically bound carbon
NO _x	=	oxides of nitrogen
NO _x -N	=	nitrogen present as oxides of nitrogen
P ₂ O ₅	=	phosphate content measured as P ₂ O ₅

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A Review of Trace Element Emissions From The Combustion of Refuse-Derived Fuel With Coal

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The effects of cocombusting refuse-derived fuel (RDF) with coal on stack emissions of trace elements in the ash stream were reviewed. The large number of variables and uncertainties involved precluded drawing definitive conclusions regarding many of the trace elements. However, it is evident that cocombustion resulted in increased emissions of Cd, Cu, Hg, Pb, and Zn. Emissions of As and Ni tended to decrease when RDF was fired with coal. Modeling studies indicated that ambient levels of trace elements during cocombustion should be within acceptable limits. However, periodic monitoring of Cd, Hg, and Pb may be warranted in some instances.

Introduction

The annual generation of municipal solid waste (MSW) was projected to be on the order of 200 million tons (1.81×10^{11} kg) by the year 1990 [1]. Due to increasingly stringent disposal regulations, rapidly decreasing landfill space, and a growing interest in energy recovery from MSW, numerous facilities have burned MSW with coal in power plants for the production of electricity. The MSW is first processed into "fluff" refuse-derived fuel (RDF), which produces a fuel consisting largely (typically 50-70%) of paper and paper products. On a dry basis, the heat content of the RDF can be as high as 7,000 Btu/lb (16,280 kJ/kg) [2, 3]. The fluff RDF is sometimes compacted into pellets or briquets to form densified RDF (d-RDF). In some rare cases, powdered RDF has been tested as a fuel supplement.

Many potentially toxic elements, such as Cd, Cr, Hg, Pb, and Zn, are enriched in RDF relative to coal. Therefore, the toxicity of the ash streams from coal/RDF combustion may be enhanced relative to ash derived from combusting coal only. In addition, the results of some studies showed that the solubility of many constituents, including Pb, increased when the ash was derived from the combustion of RDF with coal [4]. The portion of the ash passing through the emission control devices and into the ambient environment through the stack system is of particular concern. Those ash particles are the most respirable and con-

tain the highest concentrations of many elements of environmental concern, including As, Ni, Pb, Sb, Se, Zn, and V [5]. In addition, many of those elements are concentrated on the particle surfaces [6], where they are most accessible for environmental interactions.

This paper summarizes typical trends in trace element emissions that may be anticipated as a result of firing coal/RDF blends relative to firing coal alone. Trace element emissions in the ash stream released to the atmosphere from conventional coal-fired boilers are discussed, while emissions upstream from particulate control devices are beyond the scope of the paper. In assessing the data, an emphasis was placed on the elements As, Be, Cd, Cr, Co, Hg, Mn, Ni, Pb, Sb, and Se, which are included in the list of hazardous air pollutants in the 1990 amendments to the Clean Air Act [7]. However, a lack of data precluded discussions for several of those elements.

Site Descriptions

A summary of the facilities [8-20] discussed in this paper are presented in Table 1. Stoker firing was always used for d-RDF, while fluff RDF was fired in either stoker- or suspension-fired units. Emission control devices varied from the relatively low efficiency mechanical collectors to the relatively efficient electrostatic precipitators (ESPs). The nominal boiler loads and percent RDF fired for the

Table 1 - Site Descriptions for Coal/RDF Combustion Studies

Site (Reference Number)	Unit(s) Used	Steam Flow (kg/s) ^a	Type of Firing	Type of RDF	Particle Collector
Ames, IA City Power Plant [8]	7	45.4	tangential	fluff	ESP
Ames, IA City Power Plant [9,10]	5,6	12.0 15.7	stoker	fluff	multicyclone
Arlington, VA G.S.A. Virginia Heating Plant [11, 12]	4	8.8	stoker	dRDF	air plenum, multicyclone
Hagerstown, MD Maryland Correctional Institute [13]	1	9.8	stoker	dRDF	multicyclone
Madison, WI Oscar Mayer and Company [14]	5	15.7	stoker	fluff	multicyclone
Milwaukee County, WI Milwaukee County Institu- tions' Power Plant [15]	3	13.8	stoker	dRDF	mech. collector, ESP
Rochester, NY Rochester Gas and Elec- tric's Russel Station [16]	3	58.6	tangential	fluff	ESP
St. Louis, MO Union Electric Meramec Plant [17,18]	1	116	tangential	fluff	ESP
Wright-Patterson Air Force Base, OH [19,20]	1	10.1	stoker	dRDF	multicyclone

a At nominal capacity.

results reported in this paper are presented in Table 2. The variations in the percent RDF fired and the boiler load within and among studies should be noted.

Composition of Fuels

In Table 3, ratios of trace elements in RDF relative to coal at a given site are shown. Only the ratios are being reported since the purpose of this paper is to make relative comparisons between emissions from coal/RDF combustion vs. firing coal alone. The omission of a facility in Table 3 indicates either that no data were presented for the elements discussed in this paper or that spectral interferences or lack of analytical sensitivity precluded obtaining meaningful data. Although the magnitudes of the ratios varied considerably among studies, elements showing an enrichment in the RDF relative to the coal were consistent. The RDF was generally enriched in Cd, Cr, Cu, Hg, Mn, Pb, and Zn relative to coal, while the coal was generally higher in As, Ni, V, and Se. Definitive conclusions on typical fuel enrichments for some elements (for example, As) could not be made because of insufficient data. Meaningful data were generally not reported for Be, although the results of one study indicated that the ratio of the concentration of this element in RDF relative to coal was about 0.6 [15].

Sampling and Analysis

Sampling was usually performed by employing isokinetic sampling using EPA Method 5 samplers and sampling protocol. An exception was the study performed by Norton et al. [8] in which isokinetic sampling was approximated using a Source Assessment Sampling System. In that study, constant sampling flow rates (rather than precise isokinetic flow rates) were used to maintain the desired cyclone cutoff points in the sampler.

A variety of analytical techniques were used to analyze the ash samples for trace elements. These include atomic absorption, inductively-coupled plasma, spark source mass spectrometry, and x-ray fluorescence. Analytical errors can be substantial and must be taken into account when interpreting the data. However, they were not discussed in most of the studies. Depending on the analytical methods employed, anticipated accuracies can range from $\pm 5\%$ (relative) to $\pm 20\%$ or more. In some cases, reported results were considered to be only semiquantitative.

Emission Results

The units used to report emission results included ppm, $\mu\text{g}/\text{m}^3$, $\mu\text{g}/\text{MJ}$, and g/hr , thus complicating data interpretation. In view of this, reporting the results in this paper was

Table 2 - Boiler Loads and Percent RDF (Based on Heat Content) Fired for Specific Sites

Site (Reference Number)	%RDF	%Load
Ames, IA [8] (Unit 7)	0	80-100
	20	80-100
Ames, IA [9, 10] (Unit 5)	0	80
	20	80
Ames, IA [9, 10] (Unit 6)	0	80
	50	80
Arlington, VA [11, 12]	0	23-63
	6-10	38-46
Hagerstown, MD [13]	0	30-55
	20	30-55
Madison, WI [14]	0	80
	15-50	60-80
Milwaukee County, WI [15]	0	65-75
	11	65-75
Rochester, NY [16]	0	100
	8-14	100
St. Louis, MO [17]	0	88-112
	8	107
Wright-Patterson Air Force Base, OH [19, 20]	0	60
	23	60

simplified by giving only the percentage change in the concentration or emission rate of a given trace element when RDF was fired with coal. This approach is preferable since the purpose of this paper is only to make relative comparisons in emissions from coal and coal/RDF combustion.

Results of the emission tests are shown in Table 4. Results from individual tests often deviated from the mean by more than 20%, and deviations of 50% or more were not uncommon, even when the samples were collected under similar experimental conditions. In many cases, some of the elemental concentrations were near the detection limits, thus complicating interpretation of those data.

In view of the analytical and experimental uncertainties, all values were rounded to a maximum of two significant figures. The lack of an entry for a given element at a facility indicates either that the element was not determined or that satisfactory analyses could not be performed because of analytical limitations.

Based on the data as a whole, the most consistent increases in trace element emissions resulting from cocombustion appear to be for Cd, Cu, Hg, Pb, and Zn. Of those, increases in Cd, Hg, Pb, and Zn were the most prominent. These results were consistent with some incinerator studies in which the ash component of the stack effluents was most notably enriched in Cd, Hg, Pb, and Zn (21). Emissions of As and Ni tended to decrease during cocombustion. Trends for the other trace elements were either mixed or uncertain due to a lack of data or because changes were less prominent. It must be kept in mind that this paper reviews only the trace element emissions in the ash stream. This is particularly significant for As, Hg, Sb, and Se, which are largely or partially in the vapor phase in the combustion effluents. Thus, trends in the ash fraction do not necessarily reflect those for total emissions of those elements. The trends in trace element emissions were generally consistent with the trace element enrichment factors presented in Table 3. The most prominent deviations from anticipated trends were for Se at Madison and for Hg and Zn at Milwaukee County. However, since Hg and Se are largely in the vapor phase, this does not necessarily constitute an anomaly for those elements. In addition, Hg concentrations in the ash stream at Milwaukee County were near the analytical detection limit, resulting in a probable decrease in accuracy.

In some of the cocombustion studies, sampling, analytical, or mathematical errors were evident. Also, in some cases, results reported using one set of units contradicted trends observed using a different set of units. Although such contradictions are possible in view of the numerous firing parameters involved, the magnitude of the discrepancies suggested that some of the data were suspect. In such cases, the most reasonable data sets (based on detailed data evaluations) were reported in this paper.

Discussion

The trends presented in this paper for a given site do not necessarily reflect current emissions at that site or current operations of the facility in question. Many of the facilities have discontinued co-firing operations. Also, the amount of data obtained was minimal in some studies, since the goal was only to gain operating experience and to perform a

Table 3 - Ratio of Trace Element Concentrations in RDF Relative to that in Coal

	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	V	Zn	Se
Ames, IA [8]	—	—	1.5	36	—	2.3	0.7	16	—	11	—
Ames, IA [9, 10]	—	—	1.8	11	—	2.6	1	24	—	10	—
Arlington, VA [11, 12]	—	—	—	—	—	—	—	2.3	—	—	—
Hagerstown, MD [13]	0.3	—	1.6	3	—	>8	0.3	>67	0.1	40	—
Madison, WI [14]	—	6.7	4.2	—	>7	12	—	7.3	<0.2	>18	<0.4
Milwaukee Co., WI [15]	—	5.8	—	—	9.3	—	—	20	—	8.7	—
St. Louis [17]	—	63	10	15	16	—	—	28	0.5	11	<0.7

Table 4 - Percent Change in Solid Emissions During Cocombustion of RDF with Coal.^a

	As	Be	Cd	Co	Cr	Cu	Hg ^b	Mn	Ni	Pb	Sb	Se	V	Zn
Ames [8]	-5		210	0	23	10		17	17	52	83	120		50
Ames [9]														
Unit 5					3	130		-28	-44	430				92
Unit 6					310	140		110	-30	500				300
Arlington [11, 12]											270			
Hagerstown [13]	-73		>1900		-3	>85	>150	35	-3	1600				920
Madison [14]	-67		550	-60	1		>480	62		640	260	200	-75	490
Milwaukee Co. [15]		50	870				-50			64				-15
Rochester [16]	11		>100	-74	-66	65	270	92	-94	>700		-64	-14	
St. Louis [17]			88		-16	180	>170			320			14	240
Wright Patterson AFB [19, 20]										1900				1200

a A negative value indicates an emission decrease. The lack of a value for a given element indicates that either data were not reported for that element or else analytical interferences or lack of sensitivity precluded obtaining meaningful data.

b The entry for Rochester includes mercury in the gas phase as well as in the ash.

qualitative evaluation of boiler performance during cocombustion. Because sampling was minimal in many instances, reported trends may also not truly reflect normal operating conditions or typical emissions at the time the studies were conducted. Also, it must be remembered that a particular RDF composition could cause widely varying changes in the ash composition between two sites, depending on the coal composition, firing parameters, and other experimental factors.

In assessing the emissions, some of the variables which affect the results must be considered. For example, the samples were not collected far enough downstream from flow disturbances in many of the studies, which could result in unrepresentative particulate samples. In such instances, sampling at an ideal location was usually not possible. The minimal number of samples collected in some cases contributed to statistical uncertainties. Numerous other variables, such as fuel composition, boiler design, boiler load, firing parameters, types of emission control devices, percent RDF fired, RDF type (fluff or densified), analytical and sampling methodologies, and duration of tests often made it difficult to draw definitive conclusions.

Analytical uncertainties must also be considered. For example, the concentration of a particular trace element could be reported to increase from 0.1 to 0.2 ppm. In some cases, these two values would be considered to be analytically identical. This is particularly true in cases where the concentrations are near the detection limit for that element. However, it may incorrectly appear as a 100% increase in concentration if the numbers are viewed as exact, depending on the element and analytical technique employed.

Because of limited sampling statistics, site-specific variations, and numerous uncontrolled variables, compari-

son of actual emission levels among various sites is not warranted. Similarly, correlations between emission results and specific variables such as the percent RDF or percent load at a given site are difficult to make. However, interstudy comparisons are valuable for identifying trends. Because of the considerable experimental and analytical uncertainties and variables involved, only the most prominent emission trends can be considered to be statistically significant. Data interpretation was often complicated by excessive data scatter. The data scatter reflects all uncertainties and variables, including analytical and sampling errors, variations in combustion conditions, and fluctuations in composition and feed rates of the coal and RDF.

A large increase in the concentration or emission rate of a given element does not necessarily constitute a substantial increase in any health risk, since increased emissions of a given trace element may still be within acceptable environmental limits in view of atmospheric dilution. In one study, estimates of ambient air concentrations were obtained by dividing stack concentrations of various trace elements by 1,000 [22]. None of the predicted ambient concentrations exceeded the TLV for a given element. In another study, trace element impacts predicted from computer modeling were well within ambient standards for all elements showing an increase in the fly ash during coal/RDF combustion [16]. In a third study, calculations indicated that ambient Pb levels may exceed 1/100 of the TLV when RDF was fired with coal, while other trace elements that showed an increase did not appear to pose a potential risk [17].

Conclusions

The limited amount of analytical data and the lack of

stringent control of operational variables precludes drawing conclusions about the effects of any specific variable, such as boiler design, type of particulate control device, and boiler load, on trace element emissions. Trends are often not definitive in view of the sampling and analytical uncertainties as well as statistical limitations. Trace element data on RDF are minimal and can vary widely. Additional trace element analyses on RDF and coal samples from numerous sources should be performed to draw more definitive conclusions on the trace element enrichments in RDF relative to coal. Also, uniform analytical methodologies should be used to allow for more meaningful data interpretations. Additional "stack" testing for trace elements is needed to more thoroughly and accurately evaluate the effect of cocombustion of RDF with coal on emissions of trace elements.

Although it generally appears that no environmental hazards will be posed from increased emissions of trace elements during cocombustion, monitoring of Cd, Hg, and Pb may be warranted in some instances. Because many trace elements of environmental concern are most concentrated on the smaller particle sizes, it is important to control emissions of those particles to minimize the potential for adverse environmental effects.

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Aerobic Biological Activated Carbon (BAC) Treatment of a Phenolic Wastewater

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Organic removal rates achieved in the aerobic BAC process were comparable to rates typically reported for traditional aerobic fixed-film systems. When operated at organic loading rates lower than 0.03 g COD/g GAC-d and air as the oxygen source, greater than 90 percent COD removal and 99 percent phenol removal was achieved. At higher organic loading rates, oxygen limitations resulted in less than optimal performance. Observed oxygen limitations were mitigated by the use of pure oxygen. Long-term stability of operation of the BAC process was excellent with one aerobic BAC column operated under the same conditions in excess of 260 days. During that time, consistent column performance was achieved without the need to provide supplemental carbon or carbon regeneration. System biomass yields ranged from 0.05 to 0.30 g VSS/g COD removed and increased with effluent COD concentration.

Introduction

As part of a multiphase study, the biological activated carbon (BAC) process was tested to assess its applicability for treating a wastewater with high phenol concentration produced by the Durez Division of Occidental Chemical Corporation (OCC), located in North Tonawanda, New York. A sequenced anaerobic/aerobic biological activated carbon (BAC) process was conceptualized and proposed for study. As conceptualized, the goal in the first stage anaerobic BAC (AnBAC) process was to achieve significant organic biodegradation under anaerobic conditions for the purposes of reducing ultimate oxygen supply requirements, lowering biological sludge disposal costs, and production of methane gas. Results from studies conducted to assess the AnBAC process for strong liquor treatment have been published previously [1]. Because of the uncertainty in final discharge options for the anaerobically treated strong liquor, studies also were conducted to assess the

potential for an aerobic BAC to provide final treatment/polishing of the strong liquor. The goal of these studies was to assess aerobic BAC process treatment rate and efficiency as a function of organic loading when aeration was supplied by either air or pure oxygen. The purpose of this paper is to present the results of these studies.

Background

The principal mechanisms leading to organic removal in BAC processes are carbon adsorption and biodegradation. In the early stages of BAC operation, adsorption of organics on the carbon is responsible for the majority of organic removal. At steady-state, the role that GAC particles play is not understood clearly. Ultimately, however, the principal organic removal mechanism in BAC processes is biodegradation unless carbon replacement is practiced. Biodegradation and organic removal rates in BAC systems are dependent on organic concentration and empty bed

Table 1 - Operating Overview of Selected Previous BAC Studies

Author	Principal Substrate	Column Diameter cm.	Carbon Size mesh	Environ.	Study Length days	Loading g COD/g GAC-d	Rem. Eff. %
Goeddertz et al. [1]	phenol	2.5	10x16	anaerobic	> 600	0.062	91
	phenol	18	8x16	anaerobic	> 600	0.020	98
Fox et al. [2]	coal gas	10	16x20	anaerobic	> 400	0.011	95
Khan et al. [3]	phenol	5.0	10x20	anaerobic	> 700	0.015	90
Wang et al. [4]	phenol	10	16x20	anaerobic	> 900	0.019	94
Suidan et al. [5]	catechol	5.0	10x20	anaerobic	> 600	0.012	95
Kim et al. [6]	phenol	10	10x20	anaerobic	> 600	0.018	var.
Ying and Weber [7]	sucrose	5.0	16x20	aerobic	< 6	0.220	40-60
Kim and Pirbazari [8]	glucose	1.9	25x30	aerobic	< 3	0.230	20
	sucrose	1.9	25x30	aerobic	< 3	0.220	42
Andrews and Tien [9]	valeric acid	7.6	25x30	aerobic	< 4	0.138	88

contact time (EBCT) which when taken jointly represent process organic loading rate, duration of reaction. Accordingly, organic loading rate is used as the principal operational and design parameter in BAC systems.

A variety of studies have been conducted to assess the treatment potential of BAC processes. A number of these studies are compiled in Table 1 along with the various attributes of the study conditions. Based on this summary, the majority of long-term operational assessments of BAC processes have been conducted under anaerobic conditions with relatively high organic loading rates. The focus for most of these studies was to gather operational data for specific high strength wastestreams. By necessity, these types of studies required long operational periods for acclimation and stability. While anaerobic BAC treatment is not the focus of this paper, it can be seen from these studies that long-term BAC process operation is possible with excellent treatment efficiencies achieved.

Conversely, the majority of aerobic studies have been short-term with a primary focus on the mechanistic aspects of BAC operation, namely adsorption and subsequent biodegradation. In these studies, as typified by those by Ying and Weber [7], Kim and Pirbazari [8], and Andrews and Tien [9], collection of operational data has been limited generally to a week or less and compared to mechanistic predictive models to assess model validity. Additional examples of these types of studies are those conducted by Speitel and Digiano [10] and Speitel et al. [11] to determine GAC bioregeneration rates. Because of the focus of these studies, steady-state operational data were not collected.

Stensel and Leglise [12] reported operational data for a biological aerated filter bed containing activated carbon as the media. While the actual length of operation was not reported in the paper, it was implied that effluent concentrations for COD and BOD₅ reported as a function of organic loading rate were obtained after an extended period of time. During the study, between 80 and 90 percent COD removal was achieved over a loading rate range of 2.5 to 15 kg COD/m³-d. Effluent concentrations of COD and BOD₅ increased at the higher organic loading rates

investigated, which likely was a result of oxygen limitations.

Experimental Facilities and Protocol

Descriptions of the aerobic BAC reactors employed during this study are presented here. In addition, protocols for wastewater makeup, column start-up, daily operation and sampling, analytical procedures and study operation are presented.

Aerobic BAC Reactor Design

Four bench scale BAC column systems were designed and operated to accomplish the goals of this study. A schematic flow diagram of the BAC system is shown in Figure 1. The column was constructed of a 2.54 cm ID plexiglass tube with an overall length of 130 cm. Each column was divided into three zones: 1) inlet zone, where the feeding and recycle water were mixed; 2) reaction zone, which was separated from the inlet zone by a 25 mesh stainless steel screen; and 3) outlet zone, which consisted of a 5 to 15 cm water headspace. The reaction zone contained 50 g of pulverized Calgon F-300 granular activated

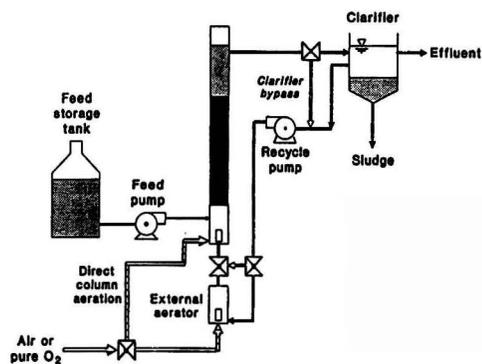


FIGURE 1. Schematic of bench-scale aerobic BAC column.

carbon (20/28 mesh).

Early in BAC column operation, detached biomass from the carbon/biomass particles in the column resulted in significant growth in the aeration tank and recycle lines. As a result, the suspended biomass concentration in the column increased causing flow restrictions in the recycle line. To mitigate these problems, a clarifier was employed before recycle. The hydraulic detention time in the clarifier ranged from 0.5 to 2.5 hours, depending on the recycle method and rate employed.

Recirculation was provided in the system to expand the carbon bed and as a means of providing oxygen. Column effluent was recycled from the clarifier as shown in Figure 1. After clarification, the recycle water was pumped to the aeration tank where it was oxygen saturated with air or pure oxygen. From the aeration tank, recycle water flowed to the column by gravity. The aeration tank had a hydraulic detention time of approximately 0.25 hours to ensure oxygen saturation in the recycle water.

To increase oxygen supply rates over those that could be achieved through recycle, direct column aeration was attempted as an auxiliary method of oxygen supply. Air was delivered into the column through a fine bubble porous diffuser located on the bottom of the column. Because of the small column diameter, only a very small amount of air could be supplied to the column before larger air bubbles were formed through coalescing of smaller bubbles. Once large bubbles were formed, carbon bridging occurred, which generally resulted in carbon spillage from the columns. As a result, direct column aeration was not employed in these studies.

Wastewater Makeup

At the time of this study, the average concentration of phenol, formaldehyde, methanol, and COD in the OCC Durez waste were 11,500 mg/L, 1,500, 1,700, and 31,100 mg/L, respectively. To achieve the expected aerobic BAC influent concentration, tap water was used to dilute strong liquor to either 200 or 400 mg/L COD. With this dilution ratio, the principal component of the feed was phenol.

A phosphate buffer consisting of KH_2PO_4 and K_2HPO_4 was used to adjust the influent pH and to provide a moderate buffer capacity. The pH in the systems was controlled at 7.0 ± 0.2 . Nitrogen requirements for biological growth were satisfied with addition of NH_4Cl . Additional nutri-

ents required for growth were satisfied by the tap water. The actual composition of the BAC influent is presented in Table 2 for an influent COD concentration of 200 mg/L. For the 400 mg/L COD feed, all ratios between COD, nitrogen, and phosphorus were held constant.

Study Protocol

Column Start-up

To initiate BAC column operation, 50 gram aliquots of prepared 20/28 mesh Calgon F-300 GAC were added to each column. Before being added to the columns, the sieved carbon had been washed with distilled water to remove fine particles, dried in a 103°C convection oven for 48 hours, and stored in capped glass bottles. After carbon addition, the columns were filled with distilled water and left idle for one day to allow degassing of the GAC.

After degassing, the carbon was presaturated with influent having a phenol concentration of 200 mg/L. The systems were then seeded with a phenol acclimated bacterial population. Acclimation was conducted in a 3 liter fill and draw batch reactor fed with diluted strong liquor daily for approximately one month. Seeding of the columns was accomplished by using 150 mL of batch reactor supernatant. After seeding, feed was initiated to the columns and daily operation begun.

Organic Loading Rate Studies

BAC process performance data was collected using organic loading as the primary operational parameter. Organic loading was varied by changes in volumetric feed rate and influent COD concentration. A range of organic loading were studied with the maximum limit being dictated by oxygen transfer and/or organic removal limitations. A single aerobic BAC column was operated under a constant organic loading rate throughout the study to evaluate the long-term carbon placement/regeneration needs and operational characteristics of BAC systems.

In the initial organic loading rate studies, compressed air was used as the oxygen source. To overcome oxygen limitations experienced with air, pure oxygen was used in later studies. When recycle lines were aerated with 99.9% purity oxygen, a dissolved oxygen concentration of 37.3 mg/L was achieved vs. 8.2 mg/L for air.

Daily Aerobic Bench BAC Column Operation

Throughout all the studies, the bench scale BAC columns were operated in an upflow expanded mode. The expansion height of the carbon bed was controlled by the recycle rate. At steady state, the carbon bed was expanded by 250 to 300 percent. Feed and recycle flow rates were checked and adjusted daily. The BAC systems were operated continuously at room temperature ($21 \pm 2^\circ\text{C}$).

To minimize the growth of biomass outside the reaction

Table 2 - Composition of Aerobic BAC Influent

Component	Concentration mg/L
Phenol	70
Formaldehyde	9
Methanol	12
COD	200
$\text{NH}_4\text{-N}$	3
$\text{PO}_4\text{-P}$	31

Table 3 - Performance Data from BAC Columns Employing Air as Oxygen Source

COD loading, g COD/g GAC-d	Flow rate L/d	Recycle ratio	Emp. Bed contact time, days	Length of operation, days	COD mg/L			Percent COD removal	Phenol mg/L			Percent phenol removal
					Inf.	Eff.	S.D.		Inf.	Eff.	S.D.	
0.020	5.1	4.9	0.031	170	194	11.5	2.8	94	72	0.3	0.2	> 99
0.025	6.5	4.0	0.025	260	194	14.8	4.1	92	72	0.4	0.5	> 99
0.034	8.7	3.0	0.019	43	194	21.0	5.9	89	72	1.6	1.1	98
0.034	8.7	5.5	0.019	98	194	21.7	3.7	89	72	1.8	0.7	97
0.045	11.5	1.9	0.014	36	194	33.4	5.0	83	72	6.3	1.5	91
0.045	11.5	4.6	0.014	60	194	30.3	6.6	84	72	4.0	1.0	94
0.045	11.5	5.8	0.014	41	194	21.3	3.5	89	72	2.2	0.9	97
0.056	14.5	2.0	0.011	90	194	42.9	9.3	78	72	8.9	2.3	88

S.D.: standard deviation

zone, routine cleaning was conducted. Aeration tanks, feed and recycle lines were cleaned with bleach once per week. The support screens on the bottom of the columns also were cleaned periodically depending on the degree of column headloss. To minimize bacterial alteration of feed character, influent feed solution was made daily and containers were cleaned with bleach before new feed was added to them.

Samples of feeding solution and effluent from each column were taken daily during the experiments. Samples were filtered through Whatman GF/C filter paper and analyzed for pH, phenol, and COD. Using separate aliquots, phenol and pH were determined immediately after sampling. COD samples were acidified to below pH 2 using concentrated sulfuric acid and stored below 4°C.

The dissolved oxygen concentration was measured in the columns and aeration tanks using membrane electrode method. Total and volatile suspended solids (TSS and VSS) concentration necessary for system yield calculations were measured by mixing solids captured in the clarifier and clarified effluent.

Analytical Procedures

Phenol analyses were conducted using spectrophotometric techniques and the 4-aminoantipyrine (4AAP) method [13]. For the spectrophotometric method, a Bausch and Lomb Spectronic 2000 with a thermoelectric flowcell was employed for spectrophotometric measurement. Phenol absorbency was measured at 270 nm and 25°C. While this method provided quick determination of phenol in relatively clean samples, biomass and biodegradation byproducts were noted to result in positive interferences in the spectrophotometric technique at low phenol concentrations. These interferences were not mitigated by simple filtration though GF/C filters. The aminoantipyrine (4AAP) method was not affected by biomass or biodegradation byproducts and thus was utilized as the definitive phenol measurement technique after biomass development. Effluent formaldehyde and methanol concentrations were not measured during the study.

The closed flux method (Standard Methods 508B) [13] was used to determine COD concentration. A Hach COD

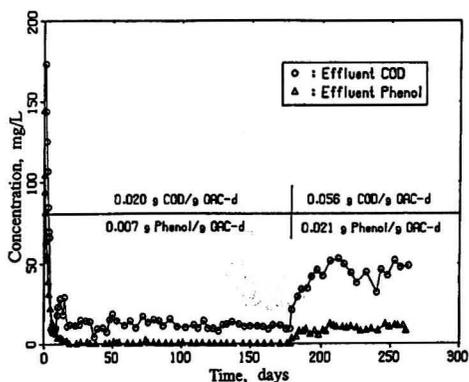


FIGURE 2. Effluent COD and phenol concentrations as a function of time at an organic loading rate of 0.020 and 0.056 g COD/g GAC-d.

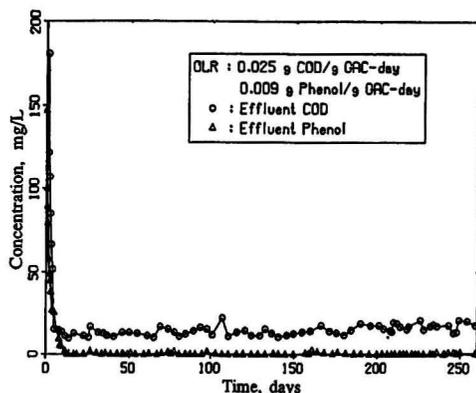


FIGURE 3. Effluent COD and phenol concentrations as a function of time and recycle rate at an organic loading rate of 0.034 g COD GAC-d.

reactor Model 16500 with 15x100 mm borosilicate screw-capped culture vials was employed for test procedure. Two ranges of digestion solutions, 0-1,500 mg/L COD and 0-150 mg/L COD, were used for the measurement of influent and effluent columns samples, respectively. Total and volatile suspended solids were measured using Standard Methods S-209C and S-209D [13], respectively.

Dissolved oxygen in the aeration tanks and columns were measured with a Model 1-8500 Neste Inst. Oxygen Meter. The DO probe was calibrated daily with oxygen saturated water.

Aerobic BAC Column Results

Column Startup

After presaturation and seeding, it took approximately 15 days for the column effluents to reach steady state with respect to effluent phenol and COD concentrations. These trends are shown in Figures 2, 3, 4, and 5 for columns operated at different loading rates. Because the columns were presaturated with a feed solution of higher phenol concentration than the influent feed used in the remainder of the study, initial effluent concentrations were higher than the influent concentration as a result of desorption. This phenomenon was short-lived and effluent concentrations were reduced quickly with concurrent biomass growth. Within two days of column initiation, biomass growth could be observed clearly and effluent turbidity increased as a result of numerous free bacteria which were observed in the effluent. By the third and fourth day, biofilm growth on the carbon surface was evident based on microscopic evaluation.

Steady-state BAC Performance

Operating conditions employed and process performance data collected during the loading rate studies are

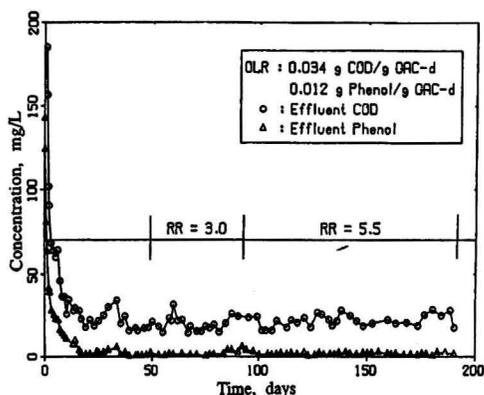


FIGURE 4. Effluent COD and phenol concentrations as a function of time and recycle rate at an organic loading rate of 0.034 g COD/g GAC-d.

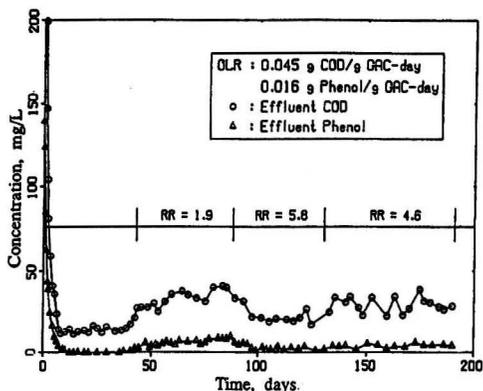


FIGURE 5. Effluent COD and Phenol concentrations as a function of time and recycle rate at an organic loading rate of 0.045 g COD/g GAC-d.

presented in Table 3. At organic loading rates of 0.020 and 0.025 g COD/g GAC-d, effluent COD concentrations averaged 11.5 and 14.8, respectively, which corresponds to removal efficiencies of 94 and 92 percent. Effluent phenol concentrations for these loading rates were below 0.5 mg/L and constitute greater than 99 percent removal. The temporal operating characteristics of columns operated at these loadings are presented in Figures 2 and 3. As shown, process performance was stable for both COD and phenol at organic loading rates of 0.020 and 0.025 g COD/g GAC-d. To provide an indication of operational stability, standard deviation for effluent COD and phenol concentrations at these loading rates are given in Table 3.

At a loading rate of 0.034 g COD/g GAC-d, two recycle

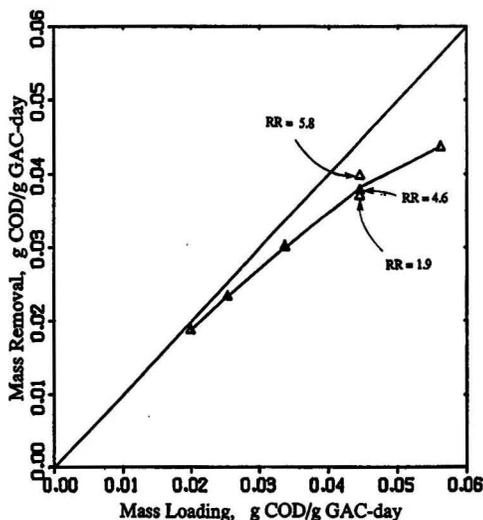


FIGURE 6. COD removal rate as a function of COD loading rate when oxygenated with air (for multiple recycle rates, the rate determined at each recycle condition is plotted.)

Table 4 - Performance Data from BAC Columns Employing Pure Oxygen as Oxygen Source

COD loading, g COD/g GAC-d	Flow rate L/d	Recycle ratio	Emp. Bed contact time, days	Length of operation, days	COD mg/L			Percent COD removal	Phenol mg/L			Percent phenol removal
					Inf.	Eff.	S.D.		Inf.	Eff.	S.D.	
0.025	6.4	5.9	0.025	16	194	17.8	1.9	91	72	bd	-	> 99
0.034	8.6	6.0	0.019	29	194	15.5	5.4	92	72	bd	-	> 99
0.044	11.3	4.2	0.014	29	194	19.8	3.6	90	72	0.5	0.6	> 99
0.056	14.3	2.9	0.011	29	194	20.9	3.7	89	72	2.0	1.0	97
0.065	8.7	3.9	0.019	8	369	25.9	4.1	93	136	4.6	2.4	96
0.085	11.5	2.8	0.014	8	369	52.7	6.8	86	136	13.5	2.8	90
0.107	14.4	3.2	0.011	8	369	72.6	3.2	80	136	18.9	2.3	86

bd: below detection limit of 0.1 mg/L
S.D.: standard deviation

rates were investigated. As shown in Figure 4 and reported in Table 3, both recycle ratios resulted in near similar performance with effluent COD concentrations averaging 21.0 and 21.7 for recycle rates of 3.0 and 5.5, respectively. Average effluent phenol concentrations were 1.6 and 1.8 mg/L, for recycle rates of 3.0 and 5.5, respectively. For both COD and phenol, there was slightly higher variation at the lower recycle rate.

The COD and phenol effluent concentrations, achieved at different recycle rates during the 0.034 g COD/g GAC-d loading, were tested to determine if they were statistically different at a 95 percent confidence level. Using the student t-test, it was found that there were no significant differences in either COD or phenol effluent concentrations as a function of recycle rate although there was a slight difference in the standard deviation. Standard deviation was greater for the lower recycle rate for COD and phenol.

Recycle rate also was varied for studies conducted at an organic loading rate of 0.045 g COD/GAC-d. The variation in effluent COD and phenol concentration as a function of recycle rate is depicted graphically in Figure 5. Effluent COD concentrations averaged 21.3, 30.3, and 33.4 mg/L for recycle rates of 5.8, 4.6, and 1.9, respectively. Effluent phenol concentrations averaged 2.2, 4.0, and 6.3 mg/L, at recycle rates of 5.8, 4.6, and 1.9, respectively. Based on the student t-test, the differences in effluent quality as a function of recycle rate are significantly different with a 95 percent confidence level. This result suggests that the BAC columns operated at the higher organic loading may be oxygen limited which could be overcome partially by increasing the oxygen supply rate through increased recycle rates.

At an organic loading rate of 0.056 g COD/g GAC-d, the highest loading rate employed with air as the oxygen source, further deterioration of effluent quality occurred as shown in Figure 2. At this loading, which was imposed on a column after 170 days of operation at a loading rate of 0.020 g COD/g GAC-d, effluent COD and phenol concentrations averaged 42.9 and 8.9 mg/L, respectively. These effluent levels correspond to removal percentages of 78

and 88 percent for COD and phenol, respectively.

Long-Term Operation

To assess the effect of long term BAC column operation, a single column was operated at a constant loading rate of 0.025 g COD/g GAC-d for more than 260 days (Figure 3). Based on these results, consistent COD and phenol removal are achievable with no carbon regeneration for long periods of BAC operation. There was variation in effluent more phenol performance as evidenced by the standard deviation/average ratios for COD and phenol which equaled 0.28 and 1.25, respectively.

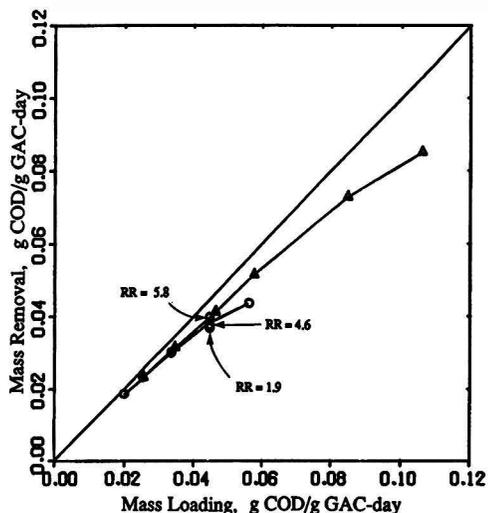


FIGURE 7. Comparison of COD removal rate as a function of COD loading rate under pure oxygen and air conditions. (For multiple recycle rates, the rate determined at each recycle condition is plotted.)

Table 5 - Solids Yield in Bench-Scale Aerobic BAC Systems

	Loading rate g COD/g GAC-d	TSS, mg/L		VSS, mg/L		VSS/TSS	Obs. Yield g VSS/g COD	
		ave.	S.D.	ave.	S.D.		ave	S.D.
Air	0.020	11.5	4.4	9.3	4.1	0.81	0.051	0.022
	0.025	24.6	10.0	20.3	8.4	0.83	0.113	0.047
	0.034	48.4	10.3	39.6	8.1	0.82	0.231	0.047
	0.045	51.6	9.3	42.6	6.8	0.83	0.253	0.040
	0.056	56.4	13.1	45.9	10.3	0.82	0.304	0.068
Pure oxygen	0.025	24.4	11.6	17.1	8.7	0.70	0.097	0.049
	0.034	28.2	8.3	19.1	6.2	0.68	0.107	0.039
	0.044	33.7	12.6	22.6	8.7	0.67	0.130	0.050
	0.056	69.1	8.4	47.0	6.6	0.68	0.272	0.038

Organic Removal

The relationship between organic loading and removal rate is plotted in Figure 6. Average concentrations of COD and influent flow rates were used in the calculation. At the lower loading rates, COD removal is essentially complete while at the higher loading rates some breakthrough is apparent. The standard deviation for organic removal rates was less than 3% for the lower organic loadings and reached as high as 5% for an organic loading rate of 0.056 g COD/g GAC-d. Based on the data presented, the maximum COD loading rate before breakthrough would appear to be between 0.03 and 0.04 g COD/g GAC-day.

Organic Supply with Pure Oxygen

Breakthrough of COD and phenol at the higher loading rates during studies conducted with air as the oxygen source was thought to be the result of limitations in oxygen supply. This belief was predicated on differences in treatment performance as a function of recycle rate which directly influenced oxygen supply. To further study oxygen limitations observed, pure oxygen was investigated as a means of increasing the oxygen supply capacity. In the pure oxygen studies, seven organic loading rates ranging from 0.025 to 0.107 g COD/g GAC-d were investigated. These rates were selected to provide some overlap with those studied when air was used as the oxygenating source. Overlap in organic loading rates was achieved between 0.025 and 0.056 g COD/g GAC-d.

Operational conditions and data collected during the pure oxygen studies are presented in Table 4. As shown, data collection periods in the pure oxygen studies were not as long as those employed during the air studies. While column biomass densities may not have reached steady-state levels during these periods for the higher organic loading rates, effluent COD and phenol concentrations were consistent and likely indicative of long-term steady-state operation.

At organic loading rates 0.025 and 0.034 g COD/g GAC-d, phenol concentration was not detectable in the

effluent and COD concentration was below 20 mg/L. These results are comparable with the results from the studies conducted with air. Effluent variation between the two oxygen sources was similar. When organic loading rates were increased to 0.044 and 0.056 g COD/g GAC-d, effluent from the pure oxygen systems was superior to that of comparably loaded air systems. Average effluent COD concentrations for these two organic loading rates were 19.8 and 20.9 mg/L and effluent phenol concentrations were 0.46 and 1.97 mg/L with typical variation in daily effluent performance. Under pure oxygen conditions, breakthrough of effluent COD and phenol was experienced when organic loading rates were higher than 0.065 g COD/g GAC-d. This breakthrough loading rate is about two times the breakthrough loading rate for air as oxygen source. These trends are demonstrated in Figure 7, which is a comparison of organic removal vs. organic loading rate achieved in the air and pure oxygen studies. The standard deviation for organic removal rate during the pure oxygen studies was less than 3% in all cases.

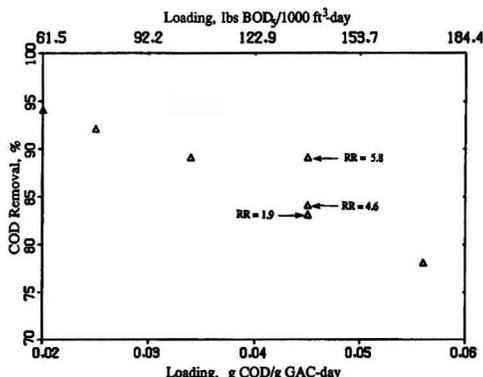


FIGURE 8. COD removal percentage as a function of organic loading rate (for multiple recycle rates, the rate determined at each recycle condition is plotted.)

Table 6 - Computation of Oxygen Deficit as a Function of Organic Loading and Aeration Procedure

	COD Loading Rate g COD/g GAC-d	COD Loading g COD/d	Eff. COD g COD/d	Obs. Yield	Oxygen Required g O ₂ /d	Recycle Flow L/day g	Oxygen Supplied O ₂ /d	Oxygen Deficit g O ₂ /d
air	0.020	0.989	0.059	0.051	0.863	25	0.205	0.658
	0.025	1.261	0.096	0.113	0.978	26	0.213	0.765
	0.034	1.688	0.183	0.231	1.012	26	0.214	0.798
	0.034	1.688	0.189	0.231	1.008	48	0.393	0.625
	0.045	2.231	0.384	0.253	1.183	22	0.179	1.004
	0.045	2.231	0.348	0.253	1.206	53	0.434	0.772
	0.045	2.231	0.245	0.253	1.273	67	0.546	0.726
	0.056	2.813	0.622	0.304	1.245	29	0.238	1.007
O ₂	0.025	1.245	0.114	0.097	0.973	38	1.404	-
	0.034	1.675	0.133	0.107	1.306	52	1.934	-
	0.044	2.200	0.224	0.130	1.608	48	1.778	-
	0.056	2.775	0.299	0.272	1.518	42	1.552	-
	0.065	3.220	0.228	0.25	1.925	34	1.266	0.659
	0.085	4.244	0.606	0.250	2.347	32	1.201	1.146
	0.107	5.314	1.045	0.250	2.740	46	1.720	1.033

BAC Sludge Yield

Sludge production was measured to estimate system biomass yields under different loading and operational conditions. To measure yield, TSS and VSS concentrations were determined for 24 hour composite samples of settled effluent and the biomass removed in the clarifier.

Average yield coefficients expressed as gram VSS produced per gram COD removed are presented in Table 5 for air and pure oxygen as oxygen sources, respectively. In addition, standard deviations for TSS, VSS, and Y_{obs} are presented.

Average observed yields in BAC systems increased with increasing loading rate. When using air as an oxygen source, the observed yield ranged from 0.051 at a loading

rate of 0.020 g COD/g GAC-d to 0.304 at loading rate 0.056 g COD/g GAC-d. Over nearly the same loading rate range (0.025 to 0.056) the pure oxygen yield varied from 0.097 to 0.272. Because of the relatively short data collection periods employed for the higher organic loading rates used during the pure oxygen studies, yield was not measured during these studies. VSS/TSS ratios were consistently higher for the air studies and averaged 0.82 as opposed to 0.68 for the pure oxygen studies.

Discussion

BAC System Operation

As demonstrated by the results of this study, aerobic

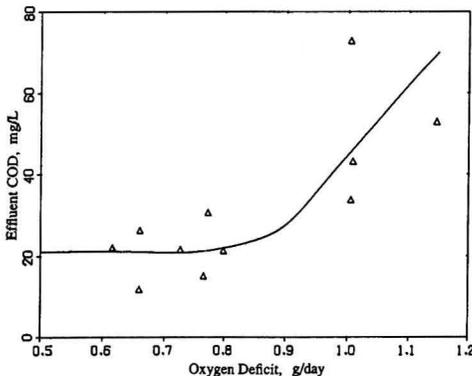


FIGURE 9. Effluent COD concentration as a function of computed oxygen deficit.

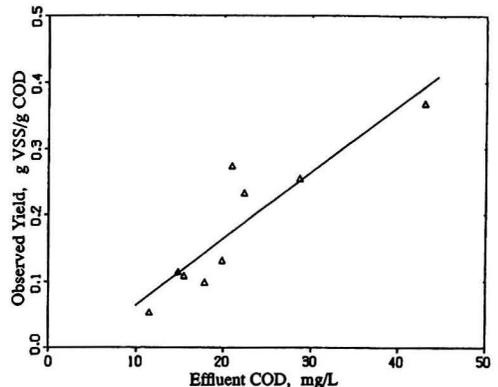


FIGURE 10. BAC system biomass yield as a function of effluent COD concentration.

BAC systems were capable of effectively degrading high phenol content wastes. When not oxygen limited by organic overloading, COD and phenol removals better than 90 and 95 percent were achieved. Start-up was rapid even though the carbon columns were presaturated and suggests that minimal start-up time would be required to place a BAC system into operation. Long-term stability of the BAC process was demonstrated under consistent loading conditions as well. Carbon replacement was not necessary to achieve stable performance in the BAC process. Elimination of supplemental carbon usage would serve to reduce the cost of BAC operation and ease operational complexity. While stable performance was achieved in this study under constant influent conditions, the aerobic BAC process also has been shown to provide excellent treatment performance under extremely variable influent conditions in pilot-scale studies conducted OCC Durez strong liquor during greater than 100 days of operation [14].

Organic Loading Rate Capacity in Aerobic BAC Systems

Organic loading and corresponding substrate removal rate typically are employed as primary parameters to define the operation of a wastewater treatment system. Historically, loading rates for fixed-film systems have been defined as the mass of substrate applied per unit time per unit volume of the reactor [15]. These units have been used for pragmatic reasons despite the fact that fixed-film processes are sensitive to media surface area which is not necessarily proportional to volume.

For conventional low and standard rate fixed-film systems, organic loading rates between 5 to 25 lbs BOD₅/1,000 ft³-d typically yield 80 to 85 percent BOD₅ removal. For high rate fixed-film systems, organic loading rates in the range of 25 to 300 lbs BOD₅/1,000 ft³-d yield 65 to 80 percent BOD₅ removal [16]. Loading rates used in this investigation, previously reported as g COD/g GAC-d, were converted to lbs COD/1,000 ft³-d using empty bed contact time as the volume and ranged from 95 to 265 lbs COD/1,000 ft³-d. Assuming that the ratio of BOD₅ to COD for this waste is 0.65, the approximate BOD₅ loading rate range applied in this study ranged from 60 to 175 BOD₅/1,000 ft³-d.

The COD removal percentages achieved as a function of organic loading rate in this study are presented in Figure 8. For ease of comparison with earlier results, percent removal is given for loading rates in units of g COD/g GAC-d and lbs BOD₅/1,000 ft³-d. As shown in Figure 8, the removal percentages achieved in this study are comparable, or slightly higher, to those reported for other high rate fixed systems.

Organic Limitations in Aerobic BAC Systems

Although excellent effluent quality was achieved at the

lower organic loading rates applied in this study, oxygen limitations were suspected throughout the BAC studies. To assess whether oxygen limitations were likely during these investigations, theoretical oxygen deficits were calculated for each organic loading rate applied. Oxygen deficits were calculated by comparing the oxygen demand rate vs. the oxygen supply rate provided by recycle. Oxygen demand rates were calculated by balancing influent and effluent soluble COD and the oxygen demand equivalent of new cell growth. For these calculations, it was assumed that each mg of dry cell material represented 1.42 mg of oxygen demand. For the purposes of the oxygen supply calculations, recycle water DO concentrations of 8.2 mg/L for air as oxygen source and 37.3 mg/L for pure oxygen were used. A summary of these calculations is provided in Table 6.

It is interesting to note that when air was employed as the oxygen source, oxygen deficits existed at all loading rates. The ratio of oxygen supplied to COD removed by aerobic oxidation was between 0.2 and 0.3 which suggests that significant anoxic biodegradation existed in the columns. When pure oxygen was used at the oxygen source, no oxygen deficits were calculated for those systems operated at low loading rates. Based on the calculated oxygen deficits, oxygen limitations were experienced during the pure oxygen studies when organic loading rates were higher than 0.065 g COD/g GAC-d.

A strong relationship between effluent COD concentration and the computed oxygen deficit was found and is shown graphically in Figure 9. When oxygen deficits were less than 0.8 g/day, insufficient supply of oxygen did not appear to adversely affect BAC column performance in terms of effluent COD. At higher oxygen deficits, effluent COD concentration appeared to increase in proportion to the oxygen deficit.

Biomass Yield

Typical biomass yields generally fall between 0.4 to 0.6 g cells/g COD removed for aerobic heterotrophs utilizing carbohydrates [14]. In fixed-film systems, biomass yield is often lower because of long mean cell residence times. In these experiments, biomass yields ranged from 0.05 to 0.37 and increased as effluent COD concentrations increased. Comparing the results of observed yields and effluent COD concentration for air and pure oxygen systems, a direct relationship between observed yield and effluent COD concentration was obtained (Figure 10).

At low organic loading rates, which resulted in low oxygen deficits and effluent concentrations, biomass growth likely was limited by substrate availability. Under low growth rate conditions caused by the substrate limitations, endogenous decay had a significant effect on biomass yield, with low biomass yields the result. At higher organic loading rates, column biodegradation rate was restricted by oxygen supply, which resulted in increased bulk fluid COD and phenol concentrations. Because of increased bulk fluid substrate concentrations, and limited oxygen conditions which would have

been most severe in the biofilm, the majority of growth occurred in the bulk fluid. This bulk fluid growth resulted in higher apparent yields.

Summary

Based on the results obtained during this study, aerobic BAC processes are capable of achieving a high quality effluent when treating the components found in the strong liquor produced by Occidental Chemical Corporation's Durez Division. Organic removal rates achieved in the BAC systems were comparable to rates typically reported for traditional aerobic fixed-film systems. When operated at organic loading rates lower than 0.03 g COD/g GAC-d and air as the oxygen source, greater than 90 percent COD removal and 99 percent phenol removal was achieved. At higher loading rates, oxygen limitations resulted in less than optimal performance.

To overcome oxygen limitations, pure oxygen and higher recycle rates were employed. When pure oxygen was used as the oxygen source, optimal performance was achieved at organic loading rates in excess of 0.05 g COD/g GAC-d. Increases in recycle rate also were found to help mitigate oxygen limitations observed during the investigation. In both the air and pure oxygen studies, COD removal rates based on oxygen demand exceeded the oxygen supply rates indicating a portion of the organic conversion achieved was brought about through anoxic and/or anaerobic biochemical pathways.

Long term stability of operation of the BAC process was excellent with one aerobic BAC column operated under the same conditions in excess of 260 days. During that time, consistent column performance was achieved without the need to provide supplemental carbon or carbon regeneration. System biomass yields ranged from 0.05 to 0.30 g VSS/g COD removed and increased with effluent COD concentration.

Acknowledgements

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Sorbent/Urea Slurry Injection for Simultaneous SO₂/NO_x Removal

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The combination of sorbent injection and selective noncatalytic reduction (SNCR) technologies has been investigated for simultaneous SO₂/NO_x removal. A slurry composed of a urea-based solution and various Ca-based sorbents was injected at a range of temperatures and reactant/pollutant stoichiometries. Testing on a natural gas pilot-scale reactor with doped pollutants achieved up to 80% reduction of SO₂ and NO_x at reactant/pollutant stoichiometric ratios of 2 and 1, respectively. SO₂ emission reductions from slurry injection were enhanced compared with dry Ca(OH)₂ sorbent injection methods possibly due to sorbent fracturing to smaller, more reactive particles. Emissions from NH₃ slip and N₂O formation were reduced in comparison with others' published results while similar NO_x reductions were obtained. The injection of the urea-based solution enhanced the SO₂ removal, likely due to the formation of a (NH₄)₂Ca(SO₄)₂•H₂O compound. The results of this pilot scale study have shown high reduction of both SO₂ and NO_x, suggesting the need for full scale studies to further assess this combined sorbent/urea-based slurry injection technology.

Introduction

Passage of the 1990 Clean Air Act Amendments has initiated extensive evaluation and planning for strategies to meet SO₂ and NO_x emission requirements. Furnace sorbent injection for SO₂ removal is a technology that has been field tested on a number of units, achieving, for example, 63% removal at a Ca/S = 2 with a calcium hydroxide [Ca(OH)₂] sorbent and 72% with a surfactant-modified Ca(OH)₂ sorbent on a 105 MW(e) wall-fired unit [1]. Lower SO₂ removals are typically achieved with calcium carbonate (CaCO₃) sorbents.

The anticipated NO_x regulations may be met, at least in part, by selective noncatalytic reduction (SNCR) which has achieved about 60% NO_x reduction on a 150 MW(e) coal boiler at a molar ratio of reductant N to initial NO_x concentration (N/NO_{x,i}) of 2 [2] and has been the subject of

numerous laboratory or pilot-scale studies [3, 4]. SNCR involves high temperature (about 800 to 1100°C) furnace injection of a N-based reducing agent such as urea (NH₂CONH₂) or ammonia (NH₃) which converts NO_x to N₂.

Most concerns with use of SNCR center around NH₃ slip resulting from incomplete reaction of the injected reductant and production of nitrous oxide (N₂O) due to incomplete reduction of NO_x. NH₃ slip can result in formation of ammonium bisulfate [(NH₄)HSO₄] around 300°C and ammonium sulfate [(NH₄)₂SO₄] around 150°C. The former can deposit upon air preheater surfaces causing reduced heat transfer and increased pressure drop. It can also cause formation of NH₄Cl around 100°C which results in a visible white plume in the stack emissions. N₂O has been implicated as a contributor to stratospheric ozone depletion [5] and global warming, the latter due to its ability to

absorb infrared radiation [6].

Research has demonstrated that levels of N_2O and NH_3 emissions from various SNCR compounds are extremely sensitive to injection temperature [7,8]. Efforts to widen the applicable temperature injection window and control NH_3 slip and N_2O production through use of additives [9] have brought about some success, yet these remain concerns that need to be addressed on any SNCR-type process.

The objective of this research was to develop the technology of simultaneous SO_2 and NO_x removal by injection of a Ca- and urea-based slurry while minimizing emissions of N_2O and NH_3 . Research on a similar SO_2/NO_x control process has shown considerable merit [10], yet significant questions still remain in the industry concerning NH_3 emissions and N_2O byproduct formation. Variables of operation included injection temperature, stoichiometric ratio, and sorbent type. Emissions monitoring results for SO_2 , NO_x , N_2O , CO, and NH_3 are reported.

Experimental

Furnace

Dry sorbent and slurry injection tests were run on a pilot-scale 14.7 kW (50,000 Btu/hr), refractory lined, down-fired cylindrical furnace capable of firing natural gas or coal. The furnace, termed the "Innovative Furnace Reactor" (IFR), has an inner diameter of 15.2 cm and an overall length of about 4 m. View and injection/probe ports traverse the length of the furnace for testing flexibility. The furnace is used to simulate the gaseous combustion environment and quench rate conditions anticipated in utility and industrial boilers. During natural gas firing, this is accomplished by doping the fuel with NH_3 (which is oxidized to form NO_x) and SO_2 . Typical operating concentrations were 600 ppm NO_x and 2,500 ppm SO_2 . The furnace was operated with tangential and axial air totalling 0.39 m^3/min STP, including an excess air of 50%.

Emissions Sampling

Gas emissions are sampled in the downstream duct section of the IFR and pass through heated sample lines to continuous emission monitors (CEMs). Analysis of SO_2 concentration by an ultraviolet analyzer follows particle traps and a heated sample line ($\approx 350^\circ C$). SO_2 removal percentages reported in this work are typically determined by running at least six tests between $Ca/S = 1$ and $Ca/S = 3$. These values are then curve fit by a regression technique and interpolated to the reported removal at $Ca/S = 2$. NO_x is analyzed by a chemiluminescent method. This method reports NO_x concentrations that do not include NO_2 ; earlier tests showed that the NO_2 concentrations were below 5% of the total NO_x concentration. All gas emission results are corrected to 0% O_2 levels.

Gases analyzed for CO_2 , O_2 , and CO were first passed

through a gas dryer and a desiccant canister of anhydrous $CaSO_4$. All of the above on-line CEMs are zeroed and spanned with gases of known concentration both before and after each daily trial.

N_2O concentrations were monitored by both on-line gas chromatography (GC) and tunable diode laser infrared (TDIR) spectroscopy methods. The GC was used for analysis of grab samples taken before and during testing using procedures in Reference 11. The TDIR was used to monitor real time stack N_2O emissions. The TDIR compares the infrared absorption of the gas sample to a known concentration of N_2O span gas at the wavelength of N_2O . This method and apparatus, which are detailed further in Reference 12, were calibrated for this work over the 20 to 80 ppm range, with an accuracy of ± 0.75 ppm. The two methods' results were comparable. Tests conducted at six varying conditions showed a linear correlation coefficient exceeding 0.99 between the two methods (for further comparison of N_2O analytical methods see Reference 13).

The analysis of stack gas NH_3 concentration was completed by wet methods using a Fisher Accumet ion selective electrode. The stack gas was drawn through an impinger system containing 0.02N H_2SO_4 . Prior to measurement, the pH was adjusted with 10M NaOH solution. The ion selective electrode, coupled with a pH meter, determines the NH_3 concentration. The meter and electrode were calibrated prior to analyses with known standards and checked throughout the testing to ensure that the values fell within the manufacturer's limits.

Sorbent/Urea Solution Injection

Testing during this work included dry sorbent injection, slurry sorbent injection, injection of two urea-based solutions with trade names $NO_xOUT A$ and $NO_xOUT A+$ (Nalco Fuel Tech), and simultaneous injection of a $NO_xOUT A$ /sorbent slurry. $NO_xOUT A$, hereafter referred to as "urea," is a urea solution including a dispersant and antiscaleant. $NO_xOUT A+$, hereafter referred to as "enhanced urea," is a urea-based solution with added reactants that shift the equilibrium point of the N_2O formation mechanism (described in Reference 8) away from the N_2O product. Tests involving injection of an NH_3 solution were included for comparison of results with those of other researchers. The sorbents tested consisted of CaO , $Ca(OH)_2$, and $CaCO_3$, all supplied by the Tenn Luttrell Company. Dry sorbent was fed by a K-Tron loss-in-weight, twin screw feeder which was calibrated prior to and after each run. Slurried sorbent at 30% solids by weight was continually mixed in a tank and metered into a Turbotak nozzle by a calibrated peristaltic pump. Baseline emission values prior to testing slurry injection were monitored while injecting an equivalent amount of deionized water (H_2O). Urea-based and NH_3 solutions were metered into the water or slurry injection by means of a calibrated dual syringe pump. A typical test scenario involved baseline

emission monitoring during H₂O injection without urea solution flow, then addition of the urea-based solution to the slurry flow, and a final return to H₂O-only injection to ensure return to baseline emission concentrations.

Both dry sorbent and slurry were injected through water-cooled probes that inject coaxially to the process gas. The dry sorbent probe injects 15.7% of the total IFR air flow to effect sorbent conveyance and dispersion. The Turbotak slurry probe uses air (18% of the total IFR air flow) to effect droplet atomization.

The slurry droplet size distribution exiting the Turbotak nozzle was determined through use of a Munhall particle size analyzer which determines droplet size by measuring diffraction of laser light. These droplet sizes were measured outside of the IFR using H₂O flow rates and pressures identical to in-furnace operation. The nozzle had a droplet size distribution with a D₅₀ of 13 μm and a D₉₀ of 88 μm. Prior to IFR testing, analysis of the slurry droplet size distribution with a spray trajectory model [14] ensured that the large droplets would not impinge on the furnace walls or remain unvaporized. Sorbent particle sizes were determined in a bench top measurement using a Micromeritics Sedigraph Model 5100.

Solid Sampling

IFR solid samples were collected isokinetically with a water-cooled sample probe. Gases passed through a particle filter and ice bath impingers, then into a dry gas meter with flow rate control to ensure isokinetic sampling. These solid samples were analyzed by x-ray diffraction to identify compounds of reaction. Diffraction analyses were run on a Siemens diffractometer with a copper Kα target source running at 50 kV and 40 mA.

Temperature Profiles

The temperature profiles through the IFR firing natural gas were determined using a suction pyrometer and a type R thermocouple. Temperatures were determined during injection of air or air/H₂O to mimic the conditions expected during dry sorbent and slurry/urea injection, respectively. The temperature at the point of the injection nozzle was calculated by extrapolation of the temperature values from downstream ports. The quench rate for natural gas firing with slurry and dry sorbent injection was nominally 240 and 293°C/s, respectively, over the range of injection ports.

Results

Sulfur Dioxide Tests

Initial tests compared the SO₂ removal of slurry vs. dry injection modes for both Ca(OH)₂ and CaCO₃. Figure 1 shows the effect of varying injection temperature upon the SO₂ removal by CaCO₃ at a Ca/S ratio of 2. The SO₂

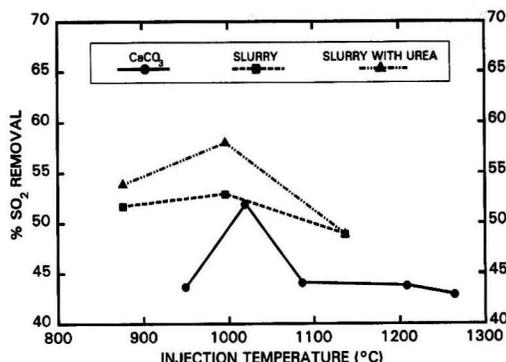


FIGURE 1. Effect of injection temperature upon SO₂ removal in CaCO₃ tests (Ca/S = 2, SO_{2i} = 2,500

removal during both dry and slurry CaCO₃ injection was fairly independent of injection temperature, given the relative error in the plotted values. Both dry and slurry injection appear to have relative maxima in SO₂ removal, about 50%, around the 1,000°C injection temperature. The addition of urea solution to the slurry water (replacing an equal volume of water) may have caused a slight increase in SO₂ capture, but insufficient runs were completed for statistical certainty.

The same tests for dry injection of Ca(OH)₂ (Figure 2) indicate that SO₂ removal, with a maximum around 1,200°C, was relatively independent of injection temperature. The slurry injection curve is similar to the dry sorbent injection curve except for a significant maximum in SO₂ removal around 1,000°C, where SO₂ capture increases to about 73%. Tests with urea addition to the slurry water mimic the temperature response of the sorbent-alone slurry, but indicate significantly higher SO₂ removal (about 10%, absolute) up to a maximum around 85% capture.

Limited tests were also done with commercially available Tenn Luttrell CaO (lime). In these tests, as-received Ca(OH)₂ was tested against a CaO slaked with the slurry injection water prior to injection. The results (also shown

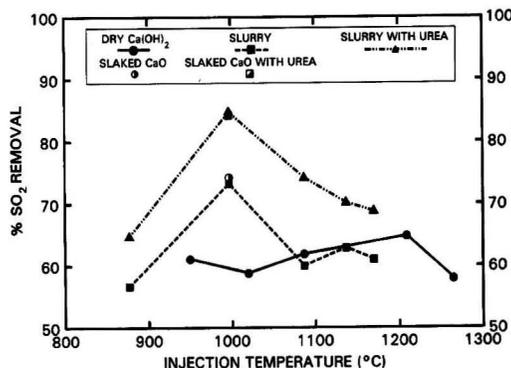


FIGURE 2. Effect of injection temperature upon SO₂ removal in Ca(OH)₂ and CaO tests (Ca/S = 2, SO_{2i} = 2,500 ppm.

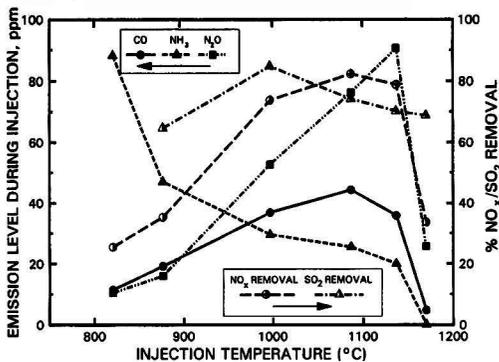


FIGURE 3. Effect of injection temperature upon emissions using urea solution ($N/NO_{xi} = 1$, $NO_{xi} = 600$ ppm).

on Figure 2) indicate that injection of a CaO slaked under nonoptimized hydration conditions yields equal SO₂ capture to the as-received Ca(OH)₂. Similarly, injection of the slaked CaO slurry with the urea solution resulted in similar capture to the as-received Ca(OH)₂ with urea, about 85% at Ca/S = 2.

Nitrogen Oxide Tests

Tests were conducted over a range of temperatures to measure the temperature sensitivity of both the urea and enhanced urea reductants. Tests varied from about 821 to 1,170°C with a N/NO_{xi} of 1 (note that urea breaks down into 2 moles of reductant N per mole of urea). The results of testing with urea, encompassing NO_x, NH₃, N₂O, and CO emissions, are shown in Figure 3. For reference, SO₂ removal results from slurry injection are superimposed on this figure, although these results were not obtained simultaneously (other results showed that the effect of concurrent sorbent injection upon NO_x removal is unnoticeable;

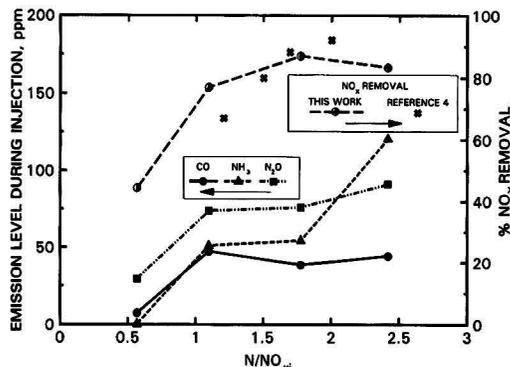


FIGURE 5. Effect of N/NO_{xi} upon emissions using urea solution (injection temperature = 997°C, $NO_{xi} = 600$ ppm) with results of Reference 4 (injection temperature = 1,100°C, $NO_{xi} = 566$ ppm).

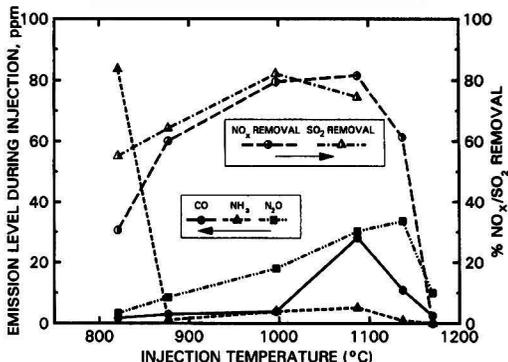


FIGURE 4. Effect of injection temperature upon emissions using enhanced urea solution ($N/NO_{xi} = 1$, $NO_{xi} = 600$ ppm).

tests with and without sorbent in the slurry did not prove to affect NO_x removals). For urea, a peak NO_x reduction of 82% is achieved at the optimum temperature of about 1,100°C, while NO_x reductions greater than 70% were obtained between injection temperatures of about 980 and 1140°C.

In comparison to these results, Figure 4 shows the results of the enhanced urea. The maximum NO_x reduction was 81% at the optimum injection temperature of around 1100°C and an N/NO_{xi} of 1. However, NO_x removals of greater than 70% were achieved at injection temperatures ranging from 930 to 1,110°C, about 50°C lower than with the urea solution.

The effect of N/NO_{xi} upon NO_x removal for urea and enhanced-urea is shown in Figures 5 and 6, respectively. NO_x removal increases with N/NO_{xi} until around an N/NO_{xi} of 1.5, where the NO_x removal starts to level off.

N₂O

N₂O emission levels (Figure 3) for urea generally

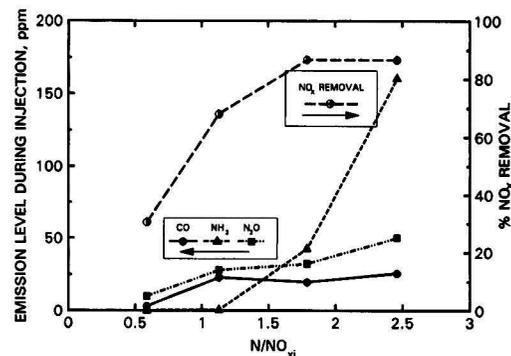


FIGURE 6. Effect of N/NO_{xi} upon emissions using enhanced urea solution (injection temperature = 997°C, $NO_{xi} = 600$ ppm).

appear to follow NO_x removal levels; peak N_2O emission (90 ppm) occurs at the same temperature as peak NO_x removal, about 1,100°C. Peak N_2O emissions using the enhanced urea (Figure 4) appear to occur about 50°C higher than the optimum injection temperature for NO_x removal. For both urea solutions, N_2O emissions follow a similar temperature response, although levels for the latter (peak value of 34 ppm) are consistently about one-third of the former.

For tests conducted near the optimum injection temperature for NO_x removal (1,087°C), increasing $\text{N}/\text{NO}_{\text{xi}}$ values results in greater N_2O emissions for both urea solutions (Figures 5 and 6, respectively). N_2O concentration ranges from 29 to 91 ppm for an $\text{N}/\text{NO}_{\text{xi}}$ of 0.5 to 2, respectively, for urea. The enhanced urea appears to be less sensitive to $\text{N}/\text{NO}_{\text{xi}}$ increases, ranging from 10 to 50 ppm for $\text{N}/\text{NO}_{\text{xi}}$ values of 0.5 to 2. For both urea-based chemicals, N_2O emissions are only slightly affected by changing $\text{N}/\text{NO}_{\text{xi}}$ values between 1 and 1.5.

NH_3

NH_3 concentrations for urea injection (Figure 3) reach a maximum of 88 ppm at 821°C. Increases in injection temperature show declining concentrations with increases in injection temperature. Peak NH_3 levels of 83 ppm for the enhanced urea (Figure 4) at 821°C are reduced below 5 ppm at injection temperatures of 887°C and higher.

Changes in $\text{N}/\text{NO}_{\text{xi}}$ values affect NH_3 emissions, as seen in Figures 5 and 6. Increases in $\text{N}/\text{NO}_{\text{xi}}$ for both urea-based solutions result in higher levels of NH_3 . As with N_2O , NH_3 levels with the urea solution are only a weak function of $\text{N}/\text{NO}_{\text{xi}}$ changes from 1 to 1.5.

Discussion

Sulfur Dioxide Tests

Comparison

The SO_2 removals (≈ 40 to 50%) reported in Figure 1 for dry CaCO_3 particles (all reported SO_2 values are at $\text{Ca}/\text{S} = 2$) somewhat exceed previous results ($\approx 40\%$) for testing in this furnace [15] and others [16]. The SO_2 removal results for dry $\text{Ca}(\text{OH})_2$ sorbent injection, $\approx 62\%$, are consistent with earlier testing in this reactor [15, 17] and numerous tests by others [18]. While it is difficult to compare results between dissimilar furnaces, fuels, initial SO_2 concentrations ($\text{SO}_{2\text{i}}$), and sorbents, the results for CaCO_3 slurry injection (≈ 50 to 60% at $\text{Ca}/\text{S} = 2$) are consistent with results from Reference 19 of about 40 to 55% at $\text{Ca}/\text{S} = 2$ and four different coal/sorbent combinations. Later work [10] indicates SO_2 removals with a $\text{Ca}(\text{OH})_2$ slurry ($\text{Ca}/\text{S} = 2$) of 78%, comparable to our peak value of $\approx 74\%$.

Temperature

The results for both dry and slurry $\text{Ca}(\text{OH})_2$ injection (Figure 2) are similar to those found for dry and slurry CaCO_3 injection in that they are, with one significant exception, relatively insensitive to temperature. While greater sensitivity to injection temperature for dry sorbent injection may be observed in other facilities (see, for example, References 16 and 18), this phenomenon is a strong function of reactor quench rate; the temperature response profile of SO_2 capture becomes flatter for lower quench rates. The IFR has a fairly moderate quench rate of about 250°C/s. Results from a pilot facility [19] operating at a quench rate of 500°C/s did show greater temperature sensitivity of SO_2 capture with slurry injection. As expected with this higher quench rate, the optimum slurry injection temperature ($\approx 1,200^\circ\text{C}$) was determined to be about 150°C higher than in our work ($\approx 1,050^\circ\text{C}$).

Dry Versus Slurry Injection

The equal or greater capture by CaCO_3 slurry vs. dry injection has been attributed to particle fragmentation or delayed sintering [20]. However, the range of data on our tests is insufficient to be conclusive - certainly there is not a significant effect of slurry injection with CaCO_3 .

The levels of SO_2 removal from the upper 50% to about 70% (excluding the urea addition results) are typical for dry $\text{Ca}(\text{OH})_2$ sorbents. Significantly greater SO_2 removals (about 10%, absolute) with slurry vs. dry injection result at one temperature (1,000°C). Unfortunately, further definition of this temperature peak was impossible due to injection port limitations. The mechanism for this enhanced removal during slurry (vs. dry) injection remains speculative.

Effect of Urea

Tests with urea added to the sorbent slurry show significant improvement over the slurry alone or dry tests. Improvements in SO_2 capture exceeding 10% absolute occur throughout the 880 to 1,170°C injection range. This phenomenon was also observed [3] when testing a hydrated lime/urea mixture and comparing it with the hydrated lime alone. It was speculated that the enhancement was due to either increased sorbent surface area and porosity from urea decomposition in the sorbent crystal structure or reactions between SO_2 and urea decomposition products in the sampling system. Our results suggest, however, that the mechanism of enhancement of the sorbent's ability to capture SO_2 is likely the reaction of the sorbent and urea-based compound with SO_2 . X-ray diffraction results from IFR solid sampling during urea injection indicate, along with the expected CaSO_4 , the significant presence of

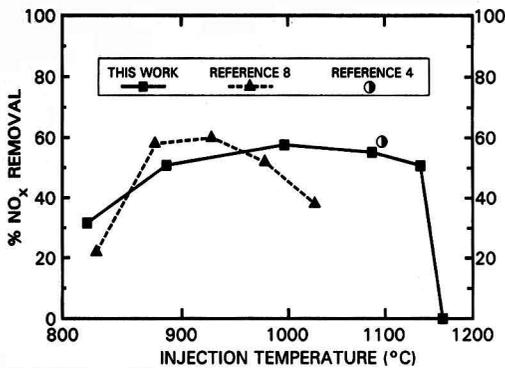


FIGURE 7. Effect of injection temperature upon NO_x removal with NH₃ solution (NO_{xi} = 600 ppm) compared with Reference 8 (NO_{xi} = 700 ppm) and Reference 4 (NO_{xi} = 619 ppm).

(NH₄)₂Ca(SO₄)₂·H₂O (kokaite). It is clear at these high temperatures, that CaO, SO₂, and the urea breakdown product (NH₃) may react together to increase SO₂ removals beyond that expected simply from the presence of CaO [from Ca(OH)₂ or CaCO₃] alone.

Ca(OH)₂ Vs. CaO Slurry

The inability to distinguish between the SO₂ reactivity of the slurries from commercially available Ca(OH)₂ vs. laboratory-slaked CaO suggests the simplicity of the hydration process towards production of reactive sorbents. Purchase costs of hydration and transportation of the added weight of H₂O in Ca(OH)₂ to the site can be avoided if CaO is mixed at the boiler site. While it is likely that improved methods of CaO slaking will increase the sorbent reactivity, our rudimentary methods of sorbent slaking were sufficient to match the results of manufacturer-supplied Ca(OH)₂.

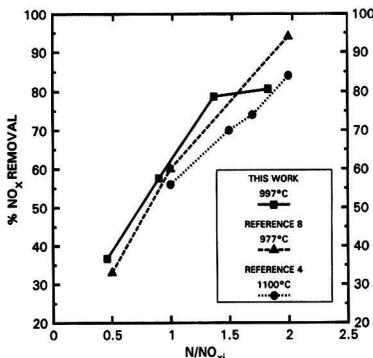


FIGURE 8. Effect of N/NO_{xi} upon NO_x removal with NH₃ solution (injection temperature = 977°C, NO_{xi} = 600 ppm) compared with Reference 8 (injection temperature = 977°C, NO_{xi} = 700 ppm) and Reference 4 (injection temperature = 1,100°C, NO_{xi} = 619 ppm).

Nitrogen Oxides Tests

Comparison

IFR test results show NO_x removals with urea at 1,000°C and varying N/NO_{xi} that are virtually identical to those demonstrated in Reference 10 under similar conditions (see Figure 5). While less similar results have been reported with urea injection by References 8 and 9, direct comparison is made tenuous by experimental differences in reductant phase (solid urea) and NO_{xi} value (250 ppm), respectively.

Tests with NH₃ solution injection were conducted to obtain data for comparison with others' results in an effort to assess any reactor-specific trends and validate the findings of this work, particularly in reference to N₂O and NH₃ emissions.

The results of NH₃ solution injection at an N/NO_{xi} of 1 are shown in Figure 7, indicating that NO_x removal exceeds 50% over a fairly broad temperature range, 887 to 1,140°C. These findings are consistent with NO_x removal results of References 4 and 8 at an N/NO_{xi} of 1. The NO_x removal response to varying the N/NO_{xi} of the NH₃ solution is shown in Figure 8, compared, likewise, with References 4 and 8.

CO emissions reported in Figures 3 through 6 are included to show the effect of injection temperature and N/NO_{xi}. These emission levels, generally 40 ppm or less, are similar to those of Reference 9. A significant increase in CO emissions at lower injection temperatures [9] is not observed, perhaps because our injection range did not extend that low.

These results indicate that reactor-specific differences in NO_x removal under similar testing conditions between these three laboratories are not significant and that results obtained in our research may apply equally well to others' reactors.

Urea Vs. Enhanced Urea

Use of enhanced urea vs. urea solution in this work improved the NO_x removal values at lower temperatures. This raises the possibility of staged injection of these chemicals at high and low temperatures, respectively. This has the additional benefit of reducing the local "load" of the nitrogen reductant injected into the flue gases, thereby minimizing potential NH₃ slip problems.

N₂O

Values of N₂O production as a function of NO_x reduction (plotted as ΔN₂O/ΔNO_x in Figure 9) for both urea-based solutions were almost exclusively less than those of References 8 and 21 with pure urea. Work reported in Reference 8 was done on a pilot-scale, natural-gas-fired combustor (described more fully in Reference 9) doped with NH₃ to produce NO_x, and Reference 21 used a pilot-scale 2 MW(t) coal-fired circulating fluidized bed. This suggests

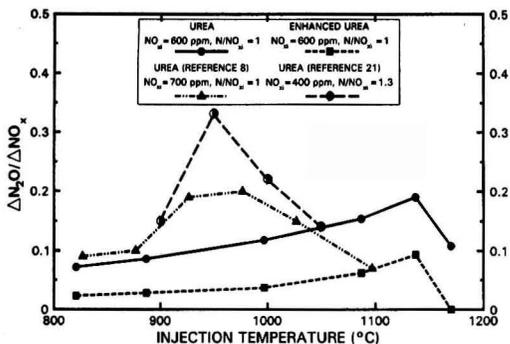


FIGURE 9. Effect of injection temperature upon N_2O emissions relative to NO_x removal compared with References 8 and 21.

that technical improvements to the pure urea solution, represented here by the urea and enhanced-urea formulations, can have an impact upon N_2O emissions in SNCR processes.

NH_3

Levels of NH_3 emissions, usually termed NH_3 "slip" in reference to the unreacted N-based reductant, for both urea-based solutions show trends of reduction with increases in temperature consistent with results of others [9]. For purposes of comparison, Figure 10 replots the NH_3 slip emissions during injection of both urea solutions with those from Reference 9. Despite a NO_{xi} level over twice that of Reference 9, NH_3 slip values in our work are significantly less throughout the full temperature range. This may likely be due to subtle differences in the experimental combustors combined with the increased reactivity of the enhanced urea formulation at lower temperatures.

Conclusions

This work has demonstrated on the pilot scale the success-

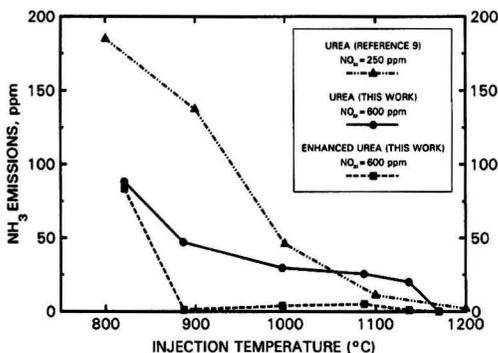


FIGURE 10. Effect of injection temperature upon NH_3 emissions at an $N/NO_{xi} = 1$ compared with Reference 9.

ful coupling of Ca-based sorbent injection and SNCR technologies in a slurry injection process. SO_2 and NO_x removals of about 70 to 80% at $Ca/S = 2$ and an $N/NO_{xi} = 1$, respectively, have been observed.

SO_2 emission control is enhanced by the combined technologies; identification of $NH_3/Ca/SO_4$ compounds suggests that the urea-based solutions react with Ca and SO_2 to effect additional SO_2 removal. Some evidence exists for the enhancement of SO_2 capture during slurry vs. dry injection of sorbents, albeit over a narrow temperature range.

Comparative levels of NH_3 and N_2O are significantly reduced below levels previously reported for urea injection through use of modified urea-based solutions. Near the peak NO_x removal levels (80%) for the enhanced urea solution ($NO_{xi} = 600$ ppm, $N/NO_{xi} = 1$), emission levels of NH_3 and N_2O were below 5 and 20 ppm, respectively.

Acknowledgements

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REQUIREMENTS FOR MEMBERSHIP

*CONSTITUTION

ARTICLE III - DEFINITION OF THE PROFESSION

Chemical engineering is the profession in which a knowledge of mathematics, chemistry and other natural sciences gained by study, experience and practice is applied with judgment to develop economic ways of using materials and energy for the benefit of mankind.

ARTICLE IV - MEMBERSHIP

Section 1. The membership of the Institute shall consist of:

(A) FELLOWS, MEMBERS, ASSOCIATE MEMBERS, AFFILIATES and STUDENT MEMBERS. A candidate for election to any grade of membership shall be engaged in an activity and possess scientific attainments or practical experience which qualify the candidate to cooperate with engineers in the advancement of chemical engineering knowledge and practice.

(B) MEMBERS shall have the exclusive privileges of representing themselves as Members, of wearing the emblem of Membership, of holding office, and of voting on amendments to this Constitution and shall also have the privileges of nominating and voting for officers and directors and the privileges that are common to all classes of membership.

(C) ASSOCIATE MEMBERS shall have the exclusive privileges of representing themselves as Associate Members and of wearing the emblem of Associate Membership and shall also have the privileges of nominating and voting for officers and directors and the privileges that are common to all classes of membership, but not the privileges of holding office and of voting on amendments to this Constitution. An Associate Member may after regular application and election become a Member.

(D) AFFILIATES shall have the exclusive privileges of representing themselves as Affiliates and of wearing the emblem of Affiliate grade of membership and shall also have the privileges that are common to all classes of membership, but not the privileges of nominating, voting, and holding office. An affiliate may, after regular application and election, become an Associate Member or Member.

Section 2. All applications for membership shall be made to the Secretary in writing, signed by the applicant, in such form and in such detail as may be prescribed by Council, and shall be referred to the Committee on Admissions.

Section 3. Election to membership shall be by vote of Council upon recommendation of the Committee on Admissions.

Section 4. An applicant shall subscribe to the Constitution and Bylaws of the Institute and its Code of Ethics upon acceptance of membership.

*From the AIChE Constitution as amended to April 1, 1989

BYLAWS**

SECTION I - MEMBERSHIP

REQUIREMENTS FOR MEMBERSHIP

Qualification for membership grade is determined by a combination of education and experience credits. An engineering school of recognized standing is one in which the engineering curriculum is accredited by the Accreditation Board for Engineering and Technology or is on the Admissions Committee's Approved List of Foreign Schools. The table below summarizes the requirements for Affiliate and Associate Membership Grades.

REQUIREMENTS FOR ASSOCIATE AND AFFILIATE MEMBERSHIP GRADES

Find in Column I a description of your education. In Column II you will see the years of chemical engineers experience required for each grade.

COLUMN I EDUCATION	COLUMN II EXPERIENCE IN CHEMICAL ENGINEERING	
	Affiliate	Associate
An earned degree in chemical engineering from a school of recognized standing	Bachelor 0 Master 0 Doctoral 0	0 0 0
An earned degree in chemical engineering from a school not of recognized standing or an earned degree in natural science or engineering other than chemical engineering from a school of recognized standing	Bachelor 0 Master 0 Doctoral 0	0+ 0+ 0+
An earned baccalaureate degree in natural science or in engineering other than chemical engineering from a school not of recognized standing	0	2
An earned baccalaureate degree in a field other than engineering or natural science	0	5
No degree	0	5

+ Must be currently practicing chemical engineering.

**From the AIChE Bylaws as amended to May 31, 1987.

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- Knowledge of new advances in transportation
- Steps to global food security and sound packaging
- Priorities of industry — what will be phased in / phased out and when

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