

ENVIRONMENTAL PROGRESS

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Environmental Considerations in Process Design and Simulation

Prepared by J. Eisenhauer and S. McQueen, Energetics Inc.

The Environmental Protection Agency, The Department of Energy, and The Center for Waste Reduction Technologies, brings a new publication which identifies how environmental factors should be incorporated into process simulation and design tools for the chemical process industries.

Authored by leading U.S. experts drawn from the industrial user community, software designers, university researchers, and federal R&D managers—this publication identifies the important R&D needed in the process simulation area and offers some perspective on R&D priorities. Ideas range from new theoretical modeling approaches being pursued in the academic community to the pragmatic data needs of process engineers who must find ways to meet environmental regulations for current operating facilities.

Issues and R&D needs addressed:

- The pertinent environmental considerations and how they should be brought into the optimization/design process
- New process models or modifications required to accommodate environmental factors in process simulation
- Current concepts of process simulators and design tools modified to incorporate environmental factors
- Data required to support process simulation and design with environmental factors

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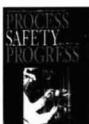
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Collaboration to Advance Environmental Technology

Jack Weaver

Director, Sponsored Research, AIChE, 345 E 47 Street, New York, N.Y. 10017

Over the past several years many attempts have been made to advance environmental technology by joining forces with other organizations both to share existing information and to sponsor new research. As many as 150 separate organizations have been formed to accomplish this, and many have achieved a great deal.

The Center for Waste Reduction Technologies (CWRT) is an example of such a collaborative group. Others that CWRT works with include the National Center for Manufacturing Sciences (NCMS), the Center for Clean Industrial & Treatment Technologies (CenCITT), and the American Institute of Pollution Prevention (AIPP).

CWRT is an industry driven, non-profit, international organization, affiliated with the American Institute of Chemical Engineers (AIChE), a professional organization. CWRT develops and transfers to industry new and innovative technologies for environmentally beneficial technologies, which CWRT defines to include waste minimization, source reduction, pollution prevention, energy and resource conservation, in-process recycle, responsible waste treatment and innovative remediation of soils and groundwater.

The Center sponsors research and development of clean, cost effective technologies and transfers this information to the user community. CWRT now has more than 25 sponsoring members including major petroleum, chemical and pharmaceutical companies, as well as other manufacturers and users of chemicals, engineering contractors, environmental consultants and government agencies. During the past year a total of nine new sponsors have joined CWRT, including the U. S. Department of Energy and the National Risk Management Research Laboratory of the U.S. Environmental Protection Agency. The activities of the center fall into three basic areas:

FUNDAMENTAL ENVIRONMENTAL RESEARCH

This includes broad research of common interest to all sponsoring members, on a variety of waste reduction technologies, including topics such as total industrial water re-use, VOC emissions reduction, integrated energy recovery and waste reduction, and integrating separations technologies with chemical reaction technology.

An innovative project has been initiated by CWRT's Research Advisory Committee to advance the concept of "separative reactors." These are operating units in which a chemical reaction and mass transfer occur simultaneously (e.g., reactive distillation, membrane reactors, PSA reactors). A public workshop is planned in 1996, involving eight or more experts, and a monograph will be published following the workshop.

APPLIED COLLABORATIVE RESEARCH

This is focused research sponsored by a smaller group of CWRT members, as well as non-members and other supporting institutions. Topics are of practical interest to the collaborating parties, with an emphasis on rapid implementation to solve real industrial problems that are vital to the collaborators.

The first "collaborative" research project to be launched by CWRT is an experimental confirmation of a novel design for a chemical reactor developed by SRI International. Six companies and the DOE are joining forces to fund this nine-month project at a total cost of over \$300,000. The six companies will cover half of the costs and DOE the remainder. The collaborating organizations will retain special rights to the technology once it is demonstrated. Up to ten additional collaborative research projects are under consideration, each project having a task force of interested sponsors actively seeking consensus on project goals and funding.

The collaborative interaction with the U.S. Department of Energy has been particularly helpful and productive. CWRT signed a cooperative agreement with DOE's Office of Industrial Technologies (OIT) just over a year ago. Since that time several projects have been initiated with matching funds from DOE. Furthermore, DOE has provided much valuable input to our planning process with their focus on source reduction, in-process recycle and energy conservation.

TECHNOLOGY TRANSFER

This includes publications, seminars and workshops, and the development of a broad family of integrated databases and analytical software for identifying and implementing source and waste reduction technologies.

In the arena of technology transfer, CWRT is funding four projects within the Clean Process Advisory System (CPASsm), a family of databases for use in the design of clean manufacturing processes. The CPASsm effort is a highly collaborative one involving not only CWRT but also CenCITT and NCMS. One of the four CPASsm projects dealing with industrial water reuse has resulted in a 150-page monograph, *How to Implement Industrial Water Reuse: A Systematic Approach*. This will be the fifth publication of CWRT, with a sixth anticipated in 1996; namely the monograph on "separative reactors".

CWRT has also prepared a "home page" on the World Wide Web, which includes a wide range of information about the Center, schedules of meetings, and other information of environmental interest. The home page can be reached at <http://cwrt.aiche.org> or <http://198.6.5.34>

Opportunities exist for many different types of collaboration in the pursuit of environmental technologies. These opportunities include collaboration between two or more companies, with industrial trade associations (such as API or CMA), with government entities (such as DOE, EPA and NIST), with professional/technical organizations, between two or more consortia (such as NCMS, CenCITT and CWRT), or various combinations of these. We should take advantage of these opportunities so that technologies can be made available to solve both public and industrial environmental problems as quickly and as cost effectively as possible.

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MONSANTO AND CWRT ANNOUNCE ONE MILLION DOLLAR ENVIRONMENTAL CHALLENGE

The Monsanto Company will team up once more with AIChE's Center for Waste Reduction Technologies (CWRT) for the Second One Million Dollar Challenge.

Monsanto will award \$1,000,000 to the individual or team that develops the most cost-effective and commercially practical technology for producing a clean sodium stream while recovering high purity amino acids and both phosphoric and phosphorous acids from a complex wastewater stream.

CWRT will work with Monsanto to facilitate the panel selection, judging criteria, and winner selection.

The technology which most effectively meets the Challenge's criteria will be funded with \$500,000 for one year of development; an additional \$500,000 will be paid following successful demonstration of the technology.

For more information and application forms, either call 1-800-366-0339 (outside North America, call (314) 213-7879) or FAX request to (314) 426-6935, or e-mail MonChalng@aol.com. All proposals must be submitted by March 31, 1996.

SURVEY FINDS "GREEN WALL" BETWEEN ENVIRONMENTAL AND BUSINESS STAFFS

A "green wall" exists between the environmental and business staffs of many companies, according to a recent survey of North American business conducted by Arthur D. Little, an international consulting company based in Cambridge, Massachusetts. According to the survey, this has created a major roadblock to managing corporate environmental issues successfully.

Managers of environment, health, and safety (EHS) at 185 corporations in the United States and Canada, representing a broad cross-section of products and services, cited two criti-

cal problems that often impede their ability to improve their companies' environmental management: a lack of integration between environmental and business issues in the company, and their own failure to convince management that environment is an important business issue. Insufficient resources was also a key factor.

More than 7 out of 10 respondents pointed to either a lack of acceptance of environmental, health, and safety by the business staff, or a separate EHS "culture" as the major roadblocks to integrating EHS functions into business. Fewer than 1 in 10 said there was no major impediment.

The remaining two out of 10 respondents cited other impediments, including:

- Organizational difficulties in aligning EHS and company business perspectives.

- Inability to show EHS as the business issue that it is, related in part to difficulties in communicating about environmental, health, and safety issues in a business context.

- Cost and resource issues, including the common problem of EHS being pigeonholed as a cost function without profit or value potential.

Only four percent of the respondents said that environmental issues are managed as part of a business team. Twenty-seven percent indicated they increasingly manage environmental issues as part of the business management decision-making responsibility.

"Getting around, over, or through the Green Wall is clearly the concern of environmental managers in a large number of companies," said Robert Shelton, director of Environmental, Health and Safety Consulting at Arthur D. Little. He noted that some industry leaders do realize that certain environmental issues are so consequential that they have the potential to affect the way a company or a whole industry does business. These companies include the environmental function as a critical part of the business process. Nevertheless, many other companies need to change, to take full advantage of the environment as a catalyst for business advantage. They must view the environment as a potential business opportunity, not just a liability.

ENVIRONMENTAL DATABASE PLUS TOLL-FREE DIRECTORY NOW AVAILABLE

A new computer phonebook listing of more than 16,000 environmental consulting and engineering firms, plus environmental organizations nationwide is now available. The database, is available on diskette in ASCII format, and is compatible with most word-processing and spreadsheet software. It is organized alphabetically and names, addresses and phone numbers for identified headquarters and branch offices are provided. The "ECO-DataPro" is updated continuously and is available on disk for \$89 or in a hard copy "traveller's edition for \$39 plus \$4 shipping and handling.

The database is produced by Paul J. Krupin, an environmental program manager with the Department of Energy's Hanford, Washington nuclear reservation. Krupin also produces the *1996 Toll-Free Environmental Directory*. In its second, expanded edition, this 152 page book lists over 7,000 toll-free "800" telephone numbers nation-wide for the entire industry spectrum of environmental organizations, consulting firms, government agencies and private institutions. Organizations, business and agencies are arranged by subject from air pollution control to water treatment.

The *1996 Toll-Free Environmental Directory* can be used on the Internet for free at <http://www.owt.com/dircon>. Cost for the book is \$14.95 plus \$4 for shipping and handling.

For more information please contact Paul Krupin at 1-800-4KRUPIN (1-800-457-8746) or write Direct Contact Publishing, P.O. Box 6726, Kennewick, Washington 99336; FAX: 1-509-582-9865; e-mail (PJ.Krupin@aol.com).

NEW FEDERAL HAZMAT RESOURCE AVAILABLE ON CD-ROM

Key findings from two critical EPA data sources are now incorporated in the new Environmental Factor RCRA Hazardous Waste Handling Information on CD-ROM from the

National Technical Information Service. From the first data source, EPA's Resource Conservation and Recovery Information System (RCRIS), users will find permit status, design capacity, and compliance history for facilities listed. From the second data source, the EPA Biennial Report System (BRS), users will find data on the waste management practice of treatment, storage and disposal facilities. With this in-depth information, the product provides the operator with cradle-to-grave waste tracking.

This CD-ROM is of special benefit to environmental consultants, hazardous waste cleanup contractors, and to managers who are actively involved in the generation, transport, storage, or disposal of hazardous waste.

The *Environmental Factor RCRA Hazardous Waste Handler Information* on CD-ROM is available from National Technical Information Service (NTIS). Telephone: (703) 487-4630 The annual cost based on three issues per year is \$2,250. To order quote order number PB96-593440KZT. For the latest issue only at \$750 please call (703) 487-4650. Please quote order number PB96-593441KZT. FAX order to (703) 321-8547. Rush service is available for an additional fee at 1-800-553-NTIS.

H2S ODOR ELIMINATED WITH CATALYTIC OXIDATION UNIT

Dissolved H2S (hydrogen sulfide) can be removed from a potable water supply by conventional air stripping methods. Nonetheless, the stripped H2S can cause serious odor problems if released into the atmosphere. The town of Jupiter, Florida solved their H2S problem by treating the air stripper emissions with a catalytic liquid oxidation unit (see photograph on the cover of this issue)

Jupiter, a community 85 miles north of Miami, found its conventional sources of fresh water insufficient to meet the needs of its growing population. Consequentially, Jupiter became the first city in Southwestern Florida to use water from the Floridan aquifer. Located 1,200 feet below the surface, the aquifer contains brackish

water contaminated with H2S. To make the water suitable for domestic use, Jupiter constructed a 6MM gpd treatment plant that includes reverse osmosis, air stripping and chemical treatment processes.

The reversed osmosis and air stripping processes successfully removed the dissolved salts and H2S, allowing the plant to produce high quality potable water. Nevertheless, during the initial operation, it was discovered that the H2S concentration of the raw water from the aquifer was greater than anticipated. This caused the H2S-laden air from the stripper to produce serious odor problems in the residential and business areas near the treatment plant.

Conventional methods for removing H2S from air streams involve wet scrubbing with chemicals such as sodium hydroxide, sodium hypochlorite, ozone solutions, etc. These scrubbing chemicals are consumed in process requiring continuous replacement. The chemicals themselves are hazardous and often produce hazardous byproducts. The continuing cost of replacing chemicals, plus the potential hazards of handling the chemicals and their byproducts, all contribute to high operating costs.

After a comprehensive study of the alternates available for H2S removal, Jupiter selected a turnkey LO-CAT oxidation system from Wheelabrator Clean Air Systems. Because of the town's immediate need for good potable water as well as good air, they required that the H2S removal system be operational within 22 weeks after contract award.

LO-CAT is a proprietary H2S treatment system that uses ferric (Fe⁺⁺⁺) ions to oxidize H2S to elemental sulfur. A chelating agent is used to tie up ferric and ferrous ions and keep them in solution.

Wheelabrator designed the system, supplied the equipment, installed it, and started it up within the 22 week requirement period. The unit met all the requirements for H2S removal. Presently, the elemental sulfur is disposed with lime waste from the water plant's softening process. The state of Florida has also approved the sulfur for direct disposal into a non-hazardous landfill.

For more information please contact Mr. Gary Nagl, Wheelabrator Clean Air Systems, 1501 E. Woodfield Road, Suite 200 West, Schamburg, IL 60173. Telephone (708) 706-6950. FAX: (708) 706-6996.

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Congress and the Environment: 1995 in Review

Prepared by AIChE's Government Relations Staff:
Dale E. Brooks and Sean Devlin Bersell

The 104th Congress convened in January of 1995 amid a great deal of enthusiasm and promises of action on a variety of environmental issues. Twelve months later, the first session of this historic Congress came to a close without enacting much legislation on environmental matters. The narrow Republican majorities in both the House and Senate meant that the GOP lacked the power to enact its environmental agenda unilaterally, and the President, after not vetoing a single bill in his first 28 months in office, vetoed 11 bills in the last seven months of 1995. Five of the bills were vetoed, at least in part, because of environmental policy disputes.

Given the current state of political discourse and the dim prospects for improvement during an election year, Congress and the President may continue to debate many of the environmental issues without coming to any final resolution this year. Rather, the voters in November will be presented with a clear choice between the two (or three) parties. They will be called upon to make a choice about the direction in which they wish the nation to go.

SUPERFUND

The failure of the President and Congress to reach agreement on a budget has eliminated the source of funds for the Superfund program and it may be difficult to reinstate it. The federal government's authority to collect the four taxes that fund the Superfund program expired at the end of 1995. The budget reconciliation bill vetoed by the President in December would have extended the taxes on petroleum, hazardous chemicals, and imported substances made with hazardous chemicals until September 30, 1996. In

addition, the corporate environmental income tax would have been extended until the end of 1996. Now that the taxes have lapsed, it may be difficult to reinstate them because of a new House rule that requires a three-fifths majority to approve new taxes.

Without the taxes, it may be even more difficult to reach agreement on Superfund reform this year. In September, Sen. Bob Smith (R-NH) released his Superfund reform bill (S. 1285), and Rep. Mike Oxley (R-OH), the chairman of one of the two House Superfund subcommittees, introduced his version of the Superfund reauthorization bill (H.R. 2500) in October. Hearings have been held on both measures. Much of the discussion at the hearings centered on the liability reform provisions of the bill, which would grant some relief from the retroactive liability provisions of the Superfund law. It would not provide the total repeal of retroactive liability that some in Congress desire. The major stumbling block to retroactive liability repeal is its cost, and the loss of the funds provided by the Superfund taxes could make it even more difficult to provide retroactive liability relief. The Oxley bill was approved by a House subcommittee in November. Nevertheless, progress on the bills in both the House and Senate has been slowed by the disputes over retroactive liability.

Both the Smith and Oxley bills include provisions embracing the "results-oriented approach" to Superfund cleanups advocated by AIChE. Sen. Smith's bill would require EPA to establish procedures for conducting response actions that "use a results-oriented approach to minimize the time required to conduct response measures and reduce the potential for exposure to the hazardous substances, pollutants, and contaminants in an

efficient, timely, and cost-effective manner." The Oxley bill states:

The President shall consider new procedures for conducting remedial investigations and feasibility studies in an efficient, cost-effective and timely manner. Such new procedures shall take into consideration a results-oriented approach in order to minimize the time required to conduct such investigations and studies.

EPA APPROPRIATIONS

Funding for the Environmental Protection Agency in Fiscal Year 1996 was passed by the Congress, but vetoed by the President. The bill contained \$5.7 billion for EPA programs, which is 14 percent less than the amount provided for Fiscal Year 1995 but greater than what either the House or Senate had initially approved. Most EPA programs would have received substantial cuts under the bill. The report accompanying the bill stated: "It must be recognized that there simply are not enough financial resources available to remedy every environmental problem that can be identified. Rather, EPA must develop serious priorities, using cost-benefit-risk analysis if appropriate, so that it can go about the task of accomplishing meaningful environmental goals in an orderly and systematic way."

One of the programs that would have seen a substantial decrease in funding under the EPA funding bill was Superfund. As passed by the Congress, the bill would have provided \$1.2 billion for Superfund in Fiscal Year 1996, a decrease of \$180 million from Fiscal Year 1995. It also would have prohibited EPA from adding sites to the National Priorities List unless requested to do so by the governor of the state in which the site is located. The proposed reduction in spending reflected Congress' hesitation to fund cleanup work—beyond that already scheduled and emergency response activities—while Congress is considering comprehensive reforms to the Superfund law.

The bill sent to the President did not include the controversial 17 "riders"—extraneous non-funding provisions—that were proposed by the House. The riders would have restricted EPA's ability to implement or enforce a host of environmental laws and regulations. The final bill did include provisions preventing EPA from issuing new drinking water

standards for radon, establishing a foreign refinery baseline for reformulated gasoline, and vetoing wetlands permits proposed to be issued by the Corps of Engineers.

The President vetoed the EPA funding bill, in part, because of its substantial reductions in environmental programs. EPA is currently funded under a temporary spending measure at the levels provided in the vetoed bill.

CLEAN WATER ACT

The House of Representatives approved a rewrite of the Clean Water Act (H.R. 961) in May by a vote of 240-185. As passed, the bill would:

- Require EPA to conduct risk assessments and cost-benefit analyses for any rules with the potential to cost more than \$25 million per year. Water quality protection programs would have to be based on scientifically objective and unbiased assessments of risks. EPA would be prohibited from issuing regulations or guidance costing more than \$25 million per year unless it can certify the rulemaking maximizes the benefits to society.

- Allow industrial sources to receive waivers from the requirement to pretreat their wastes before discharging them to a publicly owned treatment works if the industrial sources meet certain quality standards.

- Grant states flexibility in choosing the methods for controlling non-point source (run-off) water pollution.

- Establish new criteria for defining a wetland and tier the wetlands protection requirements.

The Senate has begun hearings on the Clean Water Act reauthorization and is expected to debate the bill later this year. However, Senator John Chafee (R-RI) the moderate chairman of the Senate Environment and Public Works Committee, has been critical of the House-passed bill. He has indicated that he favors a more narrow reauthorization of the Act that would make needed reforms while maintaining the safeguards included in existing law. Sen. Chafee has stated that he wants the bill to focus on funding, wetlands, storm water permitting, combined sewer overflows, polluted runoff, and watershed planning.

Sen. Chafee's position is bolstered by President Clinton, who has vowed to veto the bill as passed by the House, and by the environmental community, which has initiated a grassroots campaign against what they are calling the "dirty water bill."

In order to stir the Senate to act on the

reauthorization of the Clean Water Act, the House of Representatives included several legislative riders regarding the Clean Water Act in its version of the bill to fund EPA (H.R. 2099). The riders that would have prevented EPA from implementing or enforcing a host of Clean Water Act provisions unless the act was reauthorized. The final version of the EPA funding bill sent to the President did not include the House-passed riders, but did include a provision preventing EPA from exercising its veto authority over wetlands permits proposed to be issued by the Corps of Engineers, while allowing EPA to continue to exercise its own wetlands enforcement authority under the Clean Water Act. President Clinton, however, vetoed the EPA funding bill.

RISK AND REGULATORY REFORM

Regulatory reform legislation, which includes provisions requiring risk assessments and cost/benefit analysis for major new environmental, health, and safety regulations, was passed by the House of Representatives in March. The "Risk Assessment and Cost-Benefit Act of 1995" was incorporated in H.R. 9 (which is part of the GOP's "Contract with America"), which was passed by the House by a vote of 277-141. The risk provisions had been previously approved as H.R. 1022 by a vote of 286-141. Under the bill, every major federal rule designed to protect the environment, human health, and safety must be accompanied by an impact analysis that includes a risk assessment, a cost/benefit analysis, and an evaluation of alternatives to the regulation. No major rule may be adopted unless the agency certifies that: the required analysis is based on objective and unbiased scientific and economic evaluations of all significant and relevant information and risk assessments; the incremental risk reduction benefits of the rule will justify its costs; and the alternatives examined were less cost-effective or less flexible. The bill also establishes standards for the conduct of risk assessments by federal agencies.

Last summer, the Senate debated a similar measure—the "Comprehensive Regulatory Reform Act" (S. 343)—that would require risk assessments and cost/benefit analyses for major new environmental, health, and safety regulations. The bill was put on hold, however, after opponents prevented the Senate leadership from ending debate and bringing it to a final vote. In the autumn, the bill's supporters attempted to do an end-run around its opponents by adding a

stripped-down version of regulatory reform to the debt limit extension bill.

President Clinton vetoed that bill. Since then, the bill's supporters have been engaged in negotiations with several moderate Democrats, led by Sen. Charles Robb (D-VA), in order to gain the votes they need to bring the measure to a final vote.

The major issues in the negotiations are primarily legal rather than technical: whether the decisional criteria of the bills should supersede or supplement existing provisions of law; whether to apply their provisions to all federal agencies or just EPA and a select group of others; whether all rules or only those having a significant economic impact will be covered; how to structure peer review requirements; whether to permit judicial review of risk assessments; and whether to allow individuals to reopen past rulemakings to apply the new requirements. These issues will be central to the debate if and when the full Senate resumes consideration of the risk legislation and when House and Senate negotiators meet to resolve the differences between their two bills.

The regulatory reform bills are strongly opposed by the Clinton Administration, environmental groups, consumer organizations, and labor unions. The President says S. 343 would "force government agencies to jump through all kinds of hoops, waste time, risk lives whenever the agency acts to protect people's health and safety." An EPA analysis states that the bill would "increase costs and bureaucratic processes in the regulatory process, while making it difficult, if not impossible, to ensure that current public health protections stay in place and that future protections can be achieved." The risk assessment and cost/benefit provisions are criticized on the grounds that they would "establish requirements that future environmental rules use prescriptive, one-size-fits-all risk assessments and cost-benefit analyses, and also expand opportunities for judicial review of scientific decisions." Senate Majority Leader Robert Dole (R-KS) has accused the Clinton Administration of engaging in "scare tactics" to frighten the public.

CLEAN AIR ACT

Despite a great deal of interest in the early months of the Congress in revising some of the more controversial elements of the Clean Air Act, Congress did little tinkering with the nation's air quality law. The major change was the enactment of a

law to lift the Act's "employee commute options" requirement, which directs employers in areas with high levels of air pollution to reduce by 25 percent the number of car trips their employees make commuting to and from work. The newly enacted provision would allow individual states to decide whether to enforce the provision.

The Congress did attempt to alter some of the other requirements of the Clean Air Act through the appropriations process. As passed by the House, the appropriations bill that funds EPA contained several riders that would block Clean Air Act programs. One would have prohibited EPA from imposing sanctions if a state failed to submit an approvable operating permit program or develop a permit program for the state. Another would have denied EPA the funding to take further action on maximum achievable control technology (MACT) standards for petroleum refineries, which was proposed in July 1994. Eventually, however, only two Clean Air Act provisions were included in the bill that was presented to the President (and subsequently vetoed). One would have prevented EPA from establishing a foreign refinery baseline for reformulated gasoline (RFG) and the other addressed a local situation in Alaska. The report accompanying the compromise bill did include language expressing Congress' concern about the MACT standards for petroleum refining industry as well as reports of illness alleged to be caused by RFG.

The major development regarding the Clean Air Act last year occurred not in Congress or the EPA, but in court. In the spring, the U.S. Court of Appeals for the District of Columbia ruled that the EPA exceeded its authority in promulgating the renewable oxygenate standard that required 30 percent of the oxygenates used in RFG to come from renewable sources, e.g., ethanol.

RCRA

In addition to introducing a Superfund reform bill, Sen. Bob Smith (R-NH) has introduced a bill to revise the Resource Conservation and Recovery Act (RCRA), the federal law that governs the generation, handling, and disposal of hazardous wastes. The RCRA bill, S. 1286, would amend RCRA to create standards for recyclable materials, clarify when a substance becomes a waste, require EPA to establish national standards for exempting low-level wastes from regulation, permit EPA to establish flexible rules based on how a waste is handled ("contingent management"), and exempt remediation wastes from RCRA if the wastes are cleaned up under a federal or state cleanup plan. Sen. Smith also included the remediation provisions in his Superfund bill.

Under Rep. Oxley's Superfund reform bill (H.R. 2500), remediation wastes and remedial actions could be excluded from RCRA land disposal restrictions and pretreatment and minimum technology landfill requirements and would not trigger further permitting or facility-wide corrective action requirements. In order to be eligible for the exclusions, the cleanup plan would have to be approved by EPA or a state. States would be permitted to administer a remediation management program; if they do so, the cleanup wastes would be exempted from subtitle C of RCRA. The remedy selection criteria for Subtitle C cleanups would be required to use standards similar to the Superfund remedy selection criteria.

Sen. Trent Lott (R-MS) introduced a RCRA bill (S. 1274) that would allow remediation waste to be cleaned up under approved state remedial action programs. Any waste subject to cleanup under an approved state remedial action program would be exempt from RCRA's hazardous waste management standards.

In January of this year, the House Commerce Committee approved a bill (H.R. 2036) to eliminate the need for decharacterized wastes disposed of in surface impoundments and injection wells to meet RCRA treatment standards if they meet Clean Water Act standards. It also would relax groundwater monitoring requirements for small municipal solid waste landfills located in dry and remote areas.

Also in December, EPA issued its long-delayed proposal for a "Hazardous Waste Identification Rule" (HWIR) under RCRA. The HWIR proposal is designed to establish constituent-specific exemptions from the RCRA hazardous waste management system for low-risk wastes that are designated because they are listed under RCRA or have been mixed with, derived from, or contain hazardous wastes.

SAFE DRINKING WATER

A Safe Drinking Water Act reauthorization bill (S. 1316) was passed unanimously by the Senate late last year. The bill would make risk-reduction and cost-benefit analyses central to the process that EPA uses to set new standards for contaminants in drinking water. It also would eliminate the requirement in current law that EPA impose drinking water standards for 25 currently unregulated contaminants every three years; the requirement would be replaced by a requirement that EPA track currently unregulated contaminants and prioritize them for study and possible regulation based on the risks they pose. In addition, the bill would relieve small water systems from the requirement of monitoring drinking water for contaminants that do not occur in their region. The House has begun hearings on the bill and is expected to bring it up for a vote later this year.

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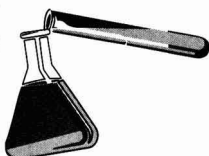
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PREVENTION AND CONTROL OF ACCIDENTAL RELEASES OF HAZARDOUS GASES

Vasilis M. Fthenakis, Van Nostrand Reinhold, New York, N.Y. (1993), 532 pages [ISBN: 0-442-00489-3], U.S. List Price: \$79.95

Of all the hazardous chemicals, gases are the most worrisome because a spill or release are a source of danger to human life. Gases spread rapidly and may, even in relatively low concentrations, pose serious health threats (depending, of course, on their composition).

In spite of best engineering efforts, chemical releases cannot be prevented. Whenever chemicals are produced, stored, or shipped, there will be accidents resulting in releases. However, it is possible to minimize the occurrence of these discharges and their impact. That is the goal of this book written by a cadre of well-known experts.

The contributors present both the practical and theoretical aspects of gas releases. In that context, they go well beyond most hazardous material texts (including one edited by this reviewer) in covering, in detail, the mathematical (theoretical) aspects of gas releases as well as mitigation procedures.

Mitigation is well covered, the editor notes, "...because there is no comprehensive text on this topic and new data have recently become available from major industrial programs. Such techniques for unconfined or partially confined releases include entraining by vapor barriers, secondary confinement or foam spraying, dispersing by water spraying, and entraining and inactivating by chemically reactive foams or liquid sprays. The theory describing the operation of these systems is discussed, and detailed procedures are presented for specific tested techniques."

The editor sets the stage by describing several severe accidental chemical releases (Bhopal, Seveso, Kerr-McGee, etc.) in the first chapter. It is followed by a chapter written by a Fellow of AIChE, Stanley Englund, on "Process and Design Options for Inherently Safer Plants." Discussed are such topics as: user-friendly plants (i.e., nonflammable versus flammable solvents), critical design review, incorporation of emergency planning in the original plant design etc.

Chapter 3 deals with the detection of hazardous gas releases. Monitoring sys-

tems for these discharges (a list of commercial gas detection devices is included) is also discussed.

Trevor Kletz, probably the best-known contributor to the literature on chemical accidents, contributed Chapter 4 entitled "Accident Prevention: Lessons Learned." Means of defense are discussed in-depth, plus the importance of (operating) procedures, and investigating accidents.

Chapters 5 and 6 are respectively entitled "Discharge Rates Through Holes in Process Vessels and Piping" and "Passive Near-Field Mitigation." It is obvious that control of gas releases is not as simple as control of liquid discharge. The question of (or partial solution to) gas discharge control is discussed in the following chapters.

Chapters 7 through 13 deal with vapor barriers; foam blanketing; foam scrubbing; water fog applications; mitigation of hydrogen fluoride aerosol clouds with water sprays, and modeling of water spraying of toxic gas releases. Containment and separation equipment for multi-phase confined releases and contaminant enclosures are discussed in Chapters 13 and 14 respectively.

The final chapters of the book deal with spill prevention. Discussed are: hazard reduction via reduced storage temperature of pressurized liquids; reliability analysis of safety systems; accident prevention guidelines and emergency preparedness and response.

This book, dealing with spill prevention preparedness and response, is most welcome. It is especially important, given the chemicals that vaporize when spilled, causing a most dangerous health hazard.

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FLOTATION SCIENCE AND ENGINEERING

K.A. Mathis, ed., Marcel Dekker, Inc., New York, N.Y. (1995), 558 pages, [ISBN: 0-8247-9264-5] U.S. List Price: \$175

Air flotation, which is an effective solids separation unit operation in mineral processing, is being increasingly utilized in the chemical process industry, especially as a selective separation technique. Many of the recent advances in the field are reviewed in this book. Unfortunately omit-

ted, and of real interest to the reader, is the treatment of oily wastewater.

The book is divided into five parts. In Part I, the fundamentals of flotation are briefly introduced with chapters on the roles of surface tension and bubble size, two of the most important variables in the process, being included. Part II focuses on the mineral processing origins of flotation. Discussed are oxide and silicate flotation, iron sulfide metal flotation, and salt-type minerals.

This reviewer was particularly interested in the four chapters that constitute Part III: Flotation Units - Cells. They were, by title:

Developments in Flotation Equipment
Residence Time Distribution in
Flotation Cells
Column Flotation
The Jameson Cell.

In Part IV, the contributors describe other successful uses of air flotation, especially in water and wastewater engineering (unfortunately, oil removal from wastewater is not included). Discussed are:

Removal of Organics from Water by
Nonfoaming Flotation
Electrolytic Flotation: An
Unconventional Technique
Flocculation in Solid-Liquid
Separation Processes
Application of the Factorial
Design to Flotation Experiments

The final section of the book is comprised of four chapters describing new applications of flotation such as biomodification of mineral surface and flotation, use of nitrogen in flotation and recovery of germanium.

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GUIDELINES FOR EVALUATING THE CHARACTERISTICS OF VAPOR CLOUD EXPLOSIONS, FLASH FIRES, AND BLEVES

Center for Chemical Process Safety (CCPS) of the AIChE, Published by the American Institute of Chemical Engineers, New York, N.Y. (1994), 387 pages, [ISBN: 0-8169-0474-X], U.S. List Price: \$150

The handbook is prepared by a team of scientists from the Explosion Prevention Department of TNO Prins Maurits labo-

ratory, Rijswijk, the Netherlands. As well as being well supplied with tables, figures and references, it provides a literature review and practical calculations for the behavior of vapor cloud explosions, flash fires and boiling liquid expanding vapor explosive (BLEVEs). Appendix F is contributed by Telmark Institute of Technology and Telemark Innovation Center, Prosgrunn, Norway.

A brief synopsis of various chapters is given in Chapter 1. There are chapters on phenomena: effects and accident scenarios; basic concepts; basic principles of vapor cloud modeling; basic principles of flash fires; basic principles of BLEVEs; BLEVEs and sample problems dealing with vapor cloud explosions, flash fires and BLEVEs.

The authors clearly indicate that not all theoretical and experimental research is covered in the book. Notwithstanding, the book can be easily used as a starting point for future research. Chapter 2 concentrates on the definition of vapor cloud explosions, flash fires and BLEVEs, plus 18 industrial accidents. Hazardous materials, severity, site characteristics, and time period are described for each industrial site accident. Basic concepts behind atmospheric vapor cloud dispersion, combustion modes, blast and thermal radiation are the subject of Chapter 3. The next chapter provides an overview of analytical and computer models on vapor cloud explosions along with the experimental research on deflagration and detonation in vapor clouds. The authors have attempted to present the material in a logical manner. Industrial managers will be able to appreciate the limitations of current approaches for solving vapor cloud explosions. Chapter 5 describes the basic research done on flash fires. The authors present a flash fire radiation model based on a literature review. A list for future research topics is given at the end of the chapter. The mechanism of a BLEVE plus methods for computing blast effects of BLEVEs and pressure-vessel bursts are dealt with in Chapter 6. The last three chapters (7 through 9) furnish solved problems on the topics discussed in the book. These chapters provide guidance on available methods and outline procedures so that engineers can apply them to their work in industry.

The book is well written and easy to understand (I could find only one typographical error). It provides an excellent overview of vapor cloud explosions, flash fires, and boiling liquid expanding

vapor explosions. It can be utilized as a text book in universities and it is also a good choice for one's personal library. The book is useful for engineers, scientists, managers and regulators interested in hazardous material.

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RISK ASSESSMENT, PRINCIPLES AND APPLICATIONS FOR HAZARDOUS WASTE AND RELATED SITES

Peter K. LaGoy, Noyes Data Corporation, Park Ridge, NJ, (1994) 248 Pages [ISBN: 0-8155-1349-6] U.S. List Price: \$ 48.00

In spite of the fact that risk assessment is playing an ever increasing role in the field of environmental remediation and control, it is still considered a "black box" by many engineers and managers responsible for remediations or for environmental control strategies. This book is a competent introduction to risk assessment and should prove useful to those individuals who work with risk assessors. It contains the information needed to work with risk assessors and to understand the meaning and limitations of a risk assessment. The book is well organized and well written. The case studies throughout the book and especially in the two appendices make the book excellent.

The book is aimed at the toxicological portion of the risk assessment process, and in general, these topics are adequately discussed. One major short-coming, in this reviewer's opinion, is the discussion on contaminant transport mechanisms via the various pathways which is limited to only about four pages in Chapter 2 and three pages in Chapter 4. This is a serious omission since the only solution to many hazardous waste cleanups is to reduce contaminant transport to acceptable levels. While detailed discussions of dispersion, groundwater, surface water, etc. are provided, modeling is beyond the scope of this book. A discussion that includes some simple calculations and explains the linear relationship between contaminant release rate and exposure for most transport pathways would be very useful.

The list of cited references is adequate (144 citations). In addition, a short bibliography is included at the end of each chap-

ter. Reference citations are current and they are adequate for the discussions of toxicological methodology such as to standardize doses for toxicological studies, but they are weak in some other areas. For example, the discussion on Toxicity Profiles includes the statement "A profile has probably been prepared for almost every chemical detected at a waste site...", but no citations where such profiles might be found are given. The book contains ten chapters and two appendices.

Chapter 1 is a short but useful introduction to the book. It's most useful feature is a standard outline for a standard baseline risk assessment. Another useful feature in this chapter is a discussion of the dual nature, scientific and policy, of the risk assessment process.

Chapter 2, "Chemical Characteristics", is a discussion of the chemical and physical properties of contaminants and of their environmental transport and fate. Because the chapter is only twelve pages long, the discussion is superficial. The chapter does include a concise list of working definitions for some commonly used terms, such as vapor pressure and octanol-water coefficient, which can be useful to a non-technical person. A list of references where such data can be obtained would have been very useful.

Chapter 3, "Regulatory Toxicology", is an excellent discussion of the interaction between scientific meaning and the uncertainties of toxicological data and the political and regulatory conclusions that one must attempt to draw from this data. The chapter gives example toxicity profiles for the following four common contaminants (or classes or contaminants) often found at contaminated sites: benzene, trans-1,2-dichloroethylene, lead, and polychlorinated dibenzodioxins and dibenzofurans (PCDDs/PCDFs). The four profiles are excellent, but references where to find other profiles would strengthen the chapter greatly.

Chapter 4, "Exposure Assessment", discusses how to estimate a population's exposure to the contaminants released from a source. The discussion is almost exclusively limited to the basic dose calculations taken from standard EPA references with no discussion or references of how one is to estimate the release rate for the contaminants. There is a short qualitative discussion of how the contaminants migrate to the environment, but there is no mention of attenuation that might be expected and how site-specific factors might increase or decrease such attenuation.

Chapter 5, "Risk Characterization", is too limited to allow calculation of a site-specific risk; however, the discussion of the actual meaning of the term "risk" is excellent. The chapter presents the advantages and limitations of the risk assessment process into a useful perspective.

Chapter 6, "Uncertainty in Risk Assessment", discusses the limits in the individual parameters which constitute a risk assessment. Most of the uncertainties are discussed in earlier chapters; this chapter consolidates the discussions.

Chapter 7, "Risk Communication", presents the general topics that should be covered when communicating the results of risk assessment to others, mainly to the general public. The chapter discusses some common pitfalls in communicating risk. A good example of one such pitfall is well discussed "...the risks posed by chemical x are far less than the risks associated with smoking one pack of cigarettes." The discussion is clear, and the ten pages of this chapter include a number of useful recommendations.

Chapter 8, "Risk Assessment as a Remediation Tool", outlines how to use the risk assessment output to establish remediation goals. The general discussion is short, but the case study given in Section 8.4 clearly illustrates how proper usage of risk assessment can be used to allocate remediation resources. The case illustrates how to use health effect estimates and their uncertainties in making cleanup decisions.

Chapter 9, "Radiation Risk Assessment", discusses risk associated with radon and with gamma radiation. The discussion is conceptual with presentation of limited dosage data. Commonly used terms related to radiation risk estimation are defined.

Chapter 10, "Ecological Risk Assessment", is a very brief discussion of the topic. This field of risk assessment is quite new so further discussion does not appear warranted at present.

The two case studies presented in Appendix A (Crop Duster Airfield) and Appendix B (Risk Assessment-Based Remediation Goals for a Metal Plating Company) in themselves justify addition of this book to a personal library. Both case studies are well organized and are quite well referenced. The discussions clearly illustrate the points being made. Each study is unique and has clearly different goals. The first case is a baseline health risk assessment to address risks to area residents. The second case study incorporates the procedures described in Chapter 8 in developing and justifying site-specific cleanup levels for

chemicals in soil and groundwater.

In conclusion, the book is a competent introduction to the field of risk assessment. It contains the information needed to work with risk assessors and to understand the meaning and limitations of a risk assessment. The book is well organized and well written. The case studies throughout the book and especially in the two appendices are excellent.

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ION EXCHANGE TECHNOLOGY: ADVANCES IN POLLUTION CONTROL

Arup K. Sengupta ed., Technomic Publishing Company, Inc., Lancaster, PA, (1995), 399 Pages [ISBN No.: 1-56676-241-3] U.S. List Price: \$89.00

With mounting regulations to ensure environmental protection coupled with efforts and initiatives on the parts of various opportunities to minimize pollution at the source, new opportunities have arisen in recent years for application of ion exchange technology. Ion exchange is a specialty sorption process; its viability for any specific application is influenced by the capacity and sorption affinity for target solutes and the regeneration or desorption efficiency. In the area of water/wastewater treatment, attention has focused on tailoring ion exchanges for achieve selective removal of trace concentrations of target contaminants. Advances in the synthesis of new ion exchange materials have also expanded the application of ion exchange technology beyond water/wastewater applications. Two examples in this regard are the removal of pollutant gases and sludge treatment by polymeric ion exchangers. Resource conservation and waste recovery have been conceptually mandated in many industrialized nations. The goal to attain "zero discharge" is a common approach in almost every industrial sector today. These societal, political, and cultural changes have warranted judicious use of selective separation technologies, for which ion exchange treatment has emerged as a viable option for many applications.

The primary intent of this book was to provide comprehensive coverage to those recent developments in ion exchange areas that continue to have major impacts in the

general pursuit of pollution control and pollution prevention. Generally, the chapters go well beyond their targeted goals, and describe the fundamentals of ion exchange, the approaches used, applications, and modeling. The book contains nine chapters written by experts in the field; these chapters can be categorized into four different theme areas: trace contaminant removal, new materials, desalination, and treatment of gaseous pollutants.

The first four chapters deal with trace contaminant removal, focusing on the treatment of waters and wastewaters contaminated with radionuclides, nitrates, chromate, and natural organic matter (NOM). The presence of naturally occurring dissolved uranium and radium compounds in arid regions on the U.S. does not allow potable use of otherwise good quality water. Nitrate is a common contaminant in many groundwaters of agricultural-intensive states. Nitrate contamination is the result of microbially mediated oxidation of ammonium-based fertilizers at the soil surface and the subsequent migration of the resultant nitrate through the subsoil strata into the groundwater. Hexavalent chromium ("chromate") is the most widely used toxic metal in many diverse industries (e.g., anodizing, electroplating, corrosion-control, oxidation, and wood treatment); chromate-contaminated groundwater is common occurrence in many areas on the U.S. Disinfection by chlorination has been a common technique for many years for producing safe drinking water. However, research during the past 20+ years has shown the presence of traces of natural organic matter (NOM) in most surface waters, upon chlorination, produces a host of cancer-causing compounds, known as trihalomethanes (THMs). NOMs are the precursors of THMs; the generation of THMs can be prevented provided traces of NOMs are removed prior to chlorination. These first four chapters provide a state-of-the-art summary for the removal of these contaminants, and emphasize how compositions of ion exchangers influence sorption affinities and regenerability.

Chapter 5 provides a detailed account of preparation methodologies, characterization techniques, equilibrium, and kinetic properties of hexacyanoferrates (HCFs) for removal of cesium. HCFs are unique for their ability to remove cesium from the background of high concentrations of alkali metals. Biomass is an environmentally renewable material and is the focus of Chapter 6. These sorbents are quite compatible with packed-bed configurations; the

guidelines for modeling and engineering design are provided in this chapter.

Chapter 7 deals with the use of ion exchange technology to deionize/demineralize fresh water with high dissolved solids (TDS) concentrations. This chapter describes the fundamentals and provides pilot-plant data for a novel ion exchange process that can partially demineralize waters with TDS concentrations as high as 3,000 mg/L. Carbon dioxide is used as the regenerant, and appears very promising for converting brackish waters for potable use.

The last two chapters describe various aspects of specific gaseous pollutants removals including the effects of resin compositions on equilibria, the prospect of cyclic packed-bed operation with temperature and pressure swings, and algorithms for modeling pollutants' effluent histories.

In summary, this book is recommended as a valuable reference source. I personally was very impressed with the thoroughness of this book, addressing both ion exchange fundamentals, modeling, and applications for treating liquid phase- and gaseous phase-pollutants. This book would be a

valuable reference source for professionals interested in separations processes, especially university researchers, regulators, consulting engineers, and plant managers.

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**POLLUTION CONTROL IN FERTILIZER
PRODUCTION**

C.A. Hodge and N. N. Popovici, eds.,
Marcel Dekker, New York, N.Y. (1994), 528
pages, [ISBN:0-8247-9188-6], U.S. List Price:
\$175.

This book is composed of a very comprehensive [although very expensive] discussion of pollution control in the fertilizer industry. After evaluating the pollution potential of this

industry, the contributors go on to present solutions capable of eliminating or diminishing pollution. They then cover methods of converting effluent and by-products to useful products.

The book consists of 39 chapters divided into the following sections:

- (1) Introduction
- (2) Nitrogen Fertilizer Industry
- (3) Phosphate Fertilizer Industry
- (4) Potassium Fertilizer Industry
- (5) Mixed Fertilizer Industry
- (6) Liquid Fertilizer Industry
- (7) Plant Site Remediation

Several contributors deal with basic chemicals that go into fertilizer production, their production, use, storage, loading, transport and pollution control. Specifically discussed are basic chemicals such as ammonia, nitric acid and phosphoric acid.

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An Overview of the U.S. EPA's Technology Transfer Network

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INTRODUCTION

The direct link between the progress of mankind and environmental degradation has led to conflicts between those who advocate hasty pollution reduction and those concerned about the potential economic impact of costly environmental controls on industry. Consequently, the need to study the impact of various contaminants on human health has gained prominence over the years. In fact, it is now mandatory for industries to check for various environmental impact scenarios before construction of a new plant or modification to an existing project.

As a consequence, computer modeling and simulations have become indispensable tools. With the astronomical advances in computer technology, the knowledge of environmental processes and its understanding has also increased tremendously. The computers serve as repositories of information enabling quick access and application for environmental projects. They are used as a decision making tool on a regular basis and during emergency planning.

In today's digital world, the key to scientific communication is information processing. The sophisticated processing modules have led to a renaissance in technology transfer from one scientific community to another. No wonder, the environmental agencies throughout the western world are focusing their attention on electronic bulletin boards on a network for exchanging information.

The Office of Air Quality Planning and Standards (abbreviated as OAQPS) at the U.S. EPA, Research Triangle Park, NC is the governing body for the dissemination of information and technology transfer for the air pollution problems in the U.S. With the help of a bulletin board system (BBS), the OAQPS provides access to the information regarding the latest developments in the field of air pollution. In addition, the BBS consists of several public domain software and a compendium of information on newsletters, federal registers, notices and conference calendars. Besides these ser-

vices, the OAQPS is also responsible for implementing the Clean Air Act.

Kumar and Manocha [1] reviewed the use of information superhighway (Internet) for obtaining environmental information. In a subsequent paper they found 12 remote sites which can be accessed using World Wide Web [2]. A list of 106 environmental bulletin board systems is provided by Kumar and Manocha [1,2]. Another list of 34 World Wide Web related sites is given in a document prepared by Air and Waste Management Association [3]. A review of five areas of environmental engineering software is given in a paper by Kumar et al [4]. Kumar and Sahore have also provided information on available software for exposure assessment modeling [5]. An insight into environmental databases is provided by Kumar and Riswadkar [6].

This paper provides the information about how to use the U.S. EPA Technology Transfer Network (referred as TTN BBS) network and a brief description of various bulletin boards available on the network. The information given on the US EPA network (TTN BBS) by Kumar and Mohan [7] will be updated in this paper.

HOW TO ACCESS THE NETWORK?

The bulletin boards listed in the U.S. EPA's Technology Transfer network can be easily accessed through the internet via telnet. The 'telnet' command allows the user to log in at remote sites. The access can be done using the following address:

Telnet TTNBBS.RTPNC.EPA.GOV

If you are logging in for the first time you need to register with the TTN BBS. On subsequent access, you will have to use the same name and password.

The other way to access the bulletin boards is by the use of modems. The communication software parameters can be set to 8 data bits, a parity of N and 1 stop bit. Then the TTN BBS be called at (919)541-5742. You gain immediate access to the electronic bulletin boards. The access is free of charge, 24 hours a day, seven days a week, except 8:00am - noon Eastern on Mondays.

STRUCTURE OF NETWORK

A table of contents is provided in the TTN BBS. This permits the user to quickly locate the needed information. The information is grouped into four major areas:

1. pollution/program services,
2. technical support services,
3. administrative support services, and
4. compliance services.

Each of these major areas are further subdivided into sub-categories. This has been explained in a tabular form in Tables I to IV.

The information available on various bulletin boards is summarized in Table V. The contact telephone numbers on important bulletin board is given in Table VI.

CONCLUDING REMARKS

The TTN BBS store a broad spectrum of factual information and data electronically. The bulletin boards are useful for the academia as well as for the environmental engineers employed in the real world. The available information can help to solve the practical problems innovatively. The software and databases available on the network are very powerful tools and are as good as any commercially available material. Although a brief description of 'What is Where' is given in this paper, we strongly recommend the readers to gain some 'hands on' experience on the use of TTN BBS.

LITERATURE CITED

1. Kumar, A and A. Manocha, "A survey of Environmental bulletin board systems", *Env. Progress*, Vol. 14, No. 1, pp F14-F16 (February 1995).
2. Kumar, A and A. Manocha, "Environmental Resources on the Internet", *Env. Progress*, Vol. 13, No. 2, pp M12-M14 (May 1994).
3. Air and Waste Management Association, "Internet Seminar", pp 47 (1995).
4. Kumar, A, S. Sahore and N. Bellam, "Environmental Software from the Flyers", *Env. Progress*, Vol. 12, No. 3, pp A8-A14 (August 1993).
5. Kumar, A and S. Sahore, "Public Domain Software for Exposure Assessment Modeling", *Env. Progress*, Vol. 13, No. 1, pp F14-F17 (February 1994).
6. Kumar, A and R. Riswadkar, "Environmental Databases", *Env. Progress*, Vol. 11, No. 2, pp M4-M15 (May 1992).
7. Kumar, A and S. Mohan, "Use of Bulletin Board System for Air Quality Modeling", *Env. Progress*, Vol. 10, No. 1, pp F8-F11 (February 1991).

Table I. Pollution program services

a) air toxics	
name	type
i) air risk information center (AIR RISC)	report/ document
ii) air/superfund coordination program	direct training
iii) crosswalk/ air toxics emission factor database	report/ document
iv) incineration-hospital waste and municipal waste	direct training
v) locating and estimating emissions from sources	report/document
vi) national air toxics information clearinghouse (NATICH)	clearing house
b) new source review/ prevention of significant deterioration	(NSR/ PSD)
name	type
i) NSR bulletin board	bulletin board
ii) NSR/PSD guidance notebook	report document
iii) NSR workshops	workshops
iv) reasonably available control technology (RACT), best available control technology(BACT), lowest achievable emission rate(LAER)	clearing house
c)operating permits	
name	type
i) model operating permit	bulletin board
ii) operating permits, question and answers	bulletin boards
iii) operating permit task force	conference
iv) operating permit workshops	workshops
v) permitting authority newsletter	newsletter
d) Ozone/ carbon monoxide/ nitrogen dioxide	
name	type
i)model VOC RACT regulations	report/document
ii) ozone control technology (CTC)	report/document
iii) ozone design value study	report/ document
iv) VOC policy guidance system	bulletin board

e) Particulate matter/ lead visibility	
name	type
i) emission sources of lead	report/document
ii) fugitive dust from agricultural sources	report/document
iii) identification of particulate matter sources of hazardous air pollutants	report/document
iv) lead guidelines	report/document
v) particulate matter (PM) guidelines	report/guidelines
vi) technical information documents on the control of residential wood combustion, prescribed burning and fugitive dust	report/document
vii) tools for locating areas with industrial sources of PM	report/document
f) sulfur dioxide	
name	type
i) sulfur dioxide guidelines	report/document
ii) sulfur dioxide yellow book	report/document

Table II. Technical Support services

a) air quality modeling	
name	type
i) air quality modeling guideline	report/document
ii) air toxic modeling	document, clearinghouse
iii) model clearinghouse	clearinghouse, report
iv) modeling workshops	workshops
v) support center for regulatory air models (SCRAM)	bulletin board
vi) surface impoundment modeling system (SIMS)	report/document
vii) use of regional oxidant model to support urban ozone modeling	computerized information transfer
b) Air quality monitoring/emissions/emission factors	
name	type
i) aerometric information retrieval system (AIRS)	conference, workgroup
ii) air emission species database (SPECIATE)	information transfer
iii) air quality trend reports	report/document

iv) ambient monitoring technology information center (AMTIC)	bulletin board
v) biogenic emissions inventory system	information transfer
vi) Clean Air Act indicators	report/document
vii) clearinghouse for inventories and emissions factors (CHIEF)	bulletin boards
viii) emission factors clearinghouse	clearinghouse
ix) emission measurement technical information center (EMTIC)	bulletin board
x) emission CD-ROM (AIR CHIEF)	information transfer
xi) national emission trends report	report/documents
xii) OAQPS/ regional office monitoring workshop	workshop
xiii) state implementation plan emission inventory PC system (SAMS)	information transfer
xiv) tools for ambient air monitoring	report/document
xv) tools for estimating air emissions	information transfer
xvi) tools for estimating ambient concentration	report/document
c) other technical support services	
name	type
i) control technology center (CTC)	bulletin board
ii) life cycle assessment program	newsletter
iii) small business assistance program (SBAP)	support center
d) Training	
name	type
i) air pollution fellowships and traineeships	direct training
ii) air pollution self-study and short courses	direct training
iii) air pollution training	direct training
iv) air pollution training institute (APTI)	bulletin board
v) air pollution videos	direct training

Table III. Administrative support services

a) General	
name	type
i) air program contacts directory	report/document
ii) Clean Air Act amendments	bulletin board

iii) directory of OAQPS information services	report/document
iv) management and accountability process system (MAPS)	bulletin board
v) OAQPS/ regional office training workshop	workshop
vi) OAQPS bulletin board systems	bulletin board
vii) work assignment guidance manual	report/document
b) Processing of state implementation plans (SIPs)	
name	type
i) SIP processing procedure manual	report/document
ii) SIP trax II	bulletin board

Table IV. Compliance services

a. Asbestos	
name	type
i) asbestos national regulatory system	conference/ workgroup
ii) asbestos program network support	conference/ workgroup
b) hazardous air pollutants (HAPs)	
name	type
i) HAP program support	report/document
c) Particulate matter (PM) / opacity	
name	type
i) PM-10 program network support	conference/workgroup
ii) reference method 9 opacity workgroup	conference/workgroup
d) Stratospheric ozone protection	
name	type
i) labeling	conference/workgroup
ii) national recycling and emission reduction program	conference/workgroup
iii) non-essential products containing chlorofluorocarbons(CFCs)	conference/workgroup
iv) phase-out production and consumption	conference/workgroup
e) Sulfur dioxide	
name	type
i) SO ₂ compliance support workgroup	conference/workgroup

f) Training	
name	type
i) advanced compliance inspector training program	conference/workgroup
ii) agency wide inspector training program workgroup	conference/workgroup
iii) federal/state/local enforcement training	clearinghouse, direct training
iv) inspector training program module development	conference/workgroup
g) Volatile organic compounds (VOCs)	
name	type
i) VOC program network support	conference/workgroup
h) Woodheaters	
name	type
i) woodheater complainece	report/document
ii) Woodheater program information	report/document

TABLE V. Description of bulletin boards on Technology Transfer Network

Item	Type	Description
1. AIRS Aerometric Information Retrieval Systems	conference/work group, bulletin board etc.	The AIRS is an integrated data system developed by EPA to replace existing databases files, and software used by EPA for storing and retrieving ambient air quality data, stationary source emission data, and facilitates compliance data. A five volume user manual is available for AIRS users. Permitting information and a permit software directory are also offered.
2. AMTIC Ambient monitoring Technology Information Center	Bulletin board , Newsletter	The AMTIC bulletin board system is centered around the exchange of information related to ambient monitoring. The system offers information on all reference and equivalent methods for criteria pollutants, federal regulations pertaining to ambient air monitoring and information related to quality assurance, quality control as well as monitoring news and field and laboratory studies of interest.
3. APTI Air Pollution Training Institute Bulletin Board system	Bulletin Board	The APTI Bulletin Board system provides complete information on all air-pollution related EPA-sponsored lectures and laboratory courses offered by the Institute. Information on course types, prerequisites, training locations, and costs are also provided.
4. BEIS Biogenic Emissions inventory Systems	Other Computerized Information transfer.	The Biogenic Emission Inventory System (BEIS) has been developed in order to allow users to estimate hourly emissions of Biogenic non methane hydrocarbons for any county in the United States.
5. CAAA Clean Air Act	Bulletin Board and Other Computerized	The CAA Bulletin Board system is designed to provide access to information on the 1990 Clean Air Amendments. Using the

Amendments	information.	bulletin board we may be able to simplify the task of complying with the requirements.
6. CHIEF Clearing House for Inventories and Emission Factors	Bulletin Board, Other Computerized Information Transfer	The CHIEF Bulletin Board system provides access to tools for estimating emissions of air pollutants and performing air emission inventories. Chief serves as EPA's central clearing house for the latest information on air emission inventories and emission factors. Emission Estimation databases, newsletters, announcements and guidance on performing inventories are included in CHIEF.
7. CTC Control Technology Center	Bulletin Board, Support Center	The CTC provides technical support in evaluating air pollution control technology applications for stationary sources. The CTC offers technical assistance on emissions and control technology applications for all air pollutants by providing easy access to EPA information and expertise. The CTC also provides access to the Federal Small Business Assistance Program (SBAP), Global Greenhouse Gases Technology Center and the RACT/ BACT/ LAER Clearinghouse (RBLC)
8. EMTIC Emission Measurement Technical Information Center	Bulletin Board, Direct Training, Newsletter, Workshop	EMTIC's newsletter, specialized workshops, and technical guidance documents provide information on measuring air pollutants (including Toxic) emissions. The EMTIC Bulletin Board system provides technical guidance on stationary source emission testing issues, particularly to people who conduct or oversee emission tests.
9. NSR New Source Review	Bulletin Board	The purpose of NSR bulletin board is to facilitate the timely transfer of up to date NSR guidance and technical information with NSR permitting community. A user of bulletin board may download or read the full text of recent NSR policy and guidance material, view summaries of past guidance material and solicit or provide information to others in a given area of new source permitting.
10. SCRAM Support Center for Regulatory Air Models	Bulletin Board, Other Computerized Information Transfer, Support Center	The SCRAM has been developed in order to implement the transfer of air quality models to the modeling community and to facilitate communications by providing a forum of ideas and information. All regulatory models including several screening models are available for retrieval by dispersion model user community. Most models are compatible with personal computers. A quarterly newsletter provides the general public with current information on SCRAM activities.
11. NATICH National Air Toxics Information Clearing House	Bulletin Board, Clearing House, Newsletter, Report	The primary purpose of NATICH is to collect, classify and disseminate air toxics information from State and Local agencies, EPA and other Federal and international agencies.
12. COMPLI Compliance Information of Stationary Sources of Air Pollution	Bulletin Board and other Computerized information	The COMPLI BBS contains three databases. The first one i.e. National Asbestos Registry System (NARS) contains a listing of all asbestos contractors, inspection and enforcement actions taken by the EPA. The second database is regarding determination Index and the third one is regarding woodstoves. It has file areas for asbestos, CFC's, PM-10, VOCs, Air Toxics.
13. OMS Mobile Source Information	BBS	The OMS provides information about the Mobile sources and associated pollution.
14. ORIA Office of Radiation and Indoor Air Information	agency BBS	The agency develops protection criteria, standards, and policies to control radiation and indoor air pollution exposures. The Office disseminates information and works with State and local governments, industry and professional groups. It has four divisions- Criteria and Standards; Radiation Studies; Radon and Indoor Air.
15. USER SUPPORT	BBS	The User Support BBS is for offering on line Hardware and software support to TTN users. They have a file library, BBS news, Tip and Tricks.
16. OTAG Ozone Transport Assessment Group	BBS	OTAG was formed for assessment of transport of Ozone and Ozone precursors (NO _x and VOC). Since no individual state or jurisdiction can be expected to either fully assess or subsequently resolve all of the issues of relevant to Ozone Transport.

TABLE VI. A List of Contact Numbers for the important bulletin boards

Bulletin Board	Contact
1. AIRS	Howard Wright (919) 541-5584, Bulletin Board (919) 541-5742
2. AMTIC	John Elkins (919) 541-5653,
3. APTI	Bulletin Board (919)541-5742
4. BEIS	Steve Beomberg (919) 541-1000
5. CAAA	Jerry Mersch (919)541-5635
6.CHEIF	Mike Hamlin (919)541-5232
7. CTC	Bob Blaszcak (919) 541-5432, Joe Steigerwald (919) 541-2736
8.EMTIC	Mike Ciolek (919)541-4931
9. NSR	Dennis Crumpler (919)541-0871
10. SCRAM	Hersch Rorex (919)541-5637
11.NATICH	Vasu Kilaru (919) 541-5332
12.COMPLI	Walter White(703)308-8704
13. OMS	Craig Harvey (313) 668-4237

Environmental Partnerships: Opportunities and Challenges

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Partnerships among business, government and environmental organizations show considerable promise for improving both the environment and the economic health of American business and industry. There is nothing more potent than a coalition of diverse interests. The author presents case studies based on his participation in partnerships involving General Motors (GM) and two environmental organizations. While environmental partnerships promise significant rewards, there are a number of challenges to be addressed, including entrenched adversarial attitudes and a regulatory paradigm that encourages business managers and government regulators alike to focus on paper "compliance" rather than real-world performance. Overcoming these challenges will require that "win/lose" and "yes/no" be replaced by "win/win" and "how to." It will require a new, market-driven paradigm that fully integrates environmental considerations into the business planning process and that relies on economic incentives to encourage business managers and government regulators to seek out real solutions to real problems.

INTRODUCTION

Partnerships among business, government and environmental organizations show considerable promise for improving both the environment and the economic health of American business and industry. There is nothing more potent than a coalition of diverse interests. The author presents case studies based on his participation in partnerships involving General Motors (GM) and two environmental organizations: the Environmental Defense Fund (EDF) and the Coalition for Environmentally Responsible Economies (CERES). While environmental partnerships promise significant rewards, there are a number of obstacles to be addressed if long-term success is to be ensured. These include the traditional adversarial nature of environmental policy deliberations and the comfort of many business people and environmental advocates with that approach. A successful partnership must be built around a set of processes and programs designed to achieve concrete, quantifiable results. This requires a new way of thinking about environmental policy and its relationship to sound business management: "win/lose" and "yes/no," must be replaced by "win/win" and "how to." Processes that fully integrate environmental considerations into the business planning process and that rely on economic incentives to encourage business managers and employees to find innovative approaches to environmental challenges are the surest way to avoid the pitfalls posed by entrenched atti-

tudes and, ultimately, to ensure the success of the environmental partnership.

Partnerships among business, government and environmental organizations show considerable promise for improving both the environment and the efficiency of American business and industry. There is nothing more powerful than a coalition of diverse interests, united to achieve a common objective. While environmental partnerships offer significant "win-win" opportunities, they also pose a number of challenges if more than good feelings and fleeting success are to be assured. The purpose of this paper is to identify some of the most attractive opportunities for partnerships, to spell out some of the most difficult challenges to making them work, and, finally, to offer some ideas for overcoming such challenges.

The author draws on his experience as a corporate economist and as a participant in two such initiatives, General Motors' dialogue with CERES, or the Coalition for Environmentally Responsible Economies and our dialogue with the Environmental Defense Fund (EDF). A third initiative, Detroit's "Ozone Action! days" grew out of the EDF/GM dialogue. Two themes common to these projects are a mutual commitment to *verifiable* environmental programs and to steady, *continuous innovation*. By "verifiability" I mean the ease with which regulators, business people and, most importantly, the general public can clearly see the environmental benefits of specific programs or policies.

THE CERES/GM DIALOGUE

Through a series of meetings among CERES and GM representatives, our CERES/GM team developed a close working relationship and a mutual commitment to certain fundamental values. General Motors' endorsement of the CERES Principles reaffirmed an ongoing commitment to our own environmental principles as an integral part of our business plan. These principles were adopted in 1991 and reaffirm a long-standing commitment that was first articulated more than three decades earlier. As a responsible corporate citizen, GM is dedicated to protecting human health, natural resources and the global environment. This dedication reaches further than compliance with the law to encompass the integration of sound environmental practices into our business decisions. The following Environmental Principles provide guidance to General Motors personnel worldwide in the conduct of their daily business practices.

1. We are committed to actions to restore and preserve the environment.
2. We are committed to reducing waste and pollutants,

conserving resources and recycling materials at every stage of the product life cycle.

3. We will continue to participate actively in educating the public regarding environmental conservation.
4. We will continue to pursue vigorously the development and implementation of technologies for minimizing pollutant emissions.
5. We will continue to work with all governmental entities for the development of technically sound and financially responsible environmental laws and regulations.
6. We will continually assess the impact of our plants and products on the environment and on the communities in which we live and operate with a goal of continuous improvement.

Endorsement of the CERES Principles underscored my company's commitment to measurable, *verifiable* environmental performance. GM now publishes an environmental report that provides our management and employees as well as the general public with information regarding GM's environmental performance—a tangible, immediate outcome of our dialogue. In the longer term, we believe that this will enhance our efforts to achieve continuous environmental *innovation*.

THE EDF/GM DIALOGUE

As an economist trained in the tradition of Adam Smith, I believe that businesses can best achieve the goals implied in our environmental principles when our engineers, designers, and marketing people are able to work with, not against market forces. It was Smith who said that individual businesses can best pursue the public interest when it is in their self interest to do so. By substituting market-pull for the push of traditional command and control regulation government policy-makers can achieve environmental objectives more effectively and more rapidly, even while enhancing the efficiency of American business and industry. That is what the Environmental Defense Fund/General Motors Dialogue has been about. From the outset, the EDF-GM working group agreed to focus on the development of economic incentive programs under the 1990 Clean Air Act Amendments. It was agreed that such an agenda would provide an opportunity to blend EDF's proven track record in designing innovative market-based environmental programs, such as the acid rain emissions trading program, with GM's know-how in economics and emissions control technology.

In principle, market-based environmental policies address pollution problems by first identifying the associated social or external costs and then by designing a set of economic incentives to "internalize" those costs within a market. If the problem is that consumers or producers of a particular good are not required to face the costs of environmental harm they impose on others, the solution is to *internalize* those costs so that each polluter now faces the costs in proportion to his or her contribution to the problem. This is not to say that market-based programs are the solution for every problem or that "market-based" means the absence of regulation. Rather, it is to say that regulations that work with market forces generally are more effective and much easier to implement than those that work against Smith's "Invisible Hand."

Market-based programs are designed to control either the price or the quantity of pollution emitted. Emissions fees (and/or subsidies) work by reflecting the costs of pollution in the prices that each polluter must pay. Emissions trading programs work by setting the allowed quantities for each polluter, together with an overall cap on total emissions, and then allowing each business to buy and sell credits achieved by over-compliance with the standards. A regulatory agency permits factories or businesses that achieve emissions reductions beyond their allocated responsibilities to create tradable credits. These businesses can then sell the credits to others who are having difficulty achieving their compliance obligations. By capping the overall level of emissions allowances, the policy makers ensure that the environmental objectives of the program are achieved. By allowing trades among the pollution sources, they are ensuring that the lowest possible cost of pollution reduction is achieved, and, most importantly, providing the affected businesses with incentives to pursue steady, continuous innovations in pollution reductions at lower and lower cost over time.

Such market-based initiatives offer substantial benefits to the environment and to the efficiency of American business and industry. For example, economists at Charles River Associates have estimated that a broadly based carbon fee, or tax on all sources of carbon dioxide in proportion to the emissions generated, could achieve any given proposed reduction in carbon dioxide at one-fiftieth the cost of a targeted reduction in new car CO₂ emissions under the Corporate Average Fuel Economy (CAFE) standard. Economists at the Environmental Defense Fund and the American Enterprise Institute have estimated that emissions trading programs can reduce stationary source pollution at less than half the cost of the most efficient command and control programs for stationary sources. By reducing the cost of compliance such programs make feasible much more ambitious programs than would otherwise be possible. That was clearly the case with the SO₂ trading program designed by the Environmental Defense Fund. Currently, trades are coming in at less than \$150 per ton¹, well below the \$500 to \$750 per ton projected by the supporters of the bill, and the \$1500 to \$2000 per ton projected by its opponents. What's more, somewhere between 2 and 6 million tons have been "over-controlled" some two years ahead of the first compliance deadline.

Our EDF/GM team's first effort was to design a market-based policy to encourage the early retirement of high-emitting vehicles, irrespective of their vintage [2]. The proposal allows stationary sources to purchase Mobile Emissions Reduction Credits (MERCs) that can be used to meet certain otherwise applicable requirements of the Clean Air Act. Consistent with our mutual commitment to the core environmental principle of verifiability, the credits are to be based on real, *measured* emissions of vehicles that will be targeted through remote-sensing devices and/or waiver lists from inspection and maintenance programs.

GM and EDF believe this program, which has been approved by the U.S. EPA, will yield guaranteed environmental benefits through the permanent retirement of ten percent of the otherwise tradable HC and NO_x net emissions reductions that result from early vehicle retirements. In the

¹"Tons" as measured in pounds—not "tonnes," as measured in kilograms.

long run, we hope that future further reductions will be realized through the precedent such flexible programs provide for the adoption of more widespread participation in emissions trading programs.

Subsequently (October 1993), in cooperation with the State of Michigan and the Michigan Department of Natural Resources (DNR), GM and EDF sponsored and led a working conference on emissions trading for the Great Lakes states. There have been several offspring of this conference, including a series of workshops on emission trading programs for Michigan, as well as Illinois, which aim to put concrete emissions trading programs into place. Recently, the Illinois EPA announced that the EDF/GM scrappage policy design will be included in its market-based implementation program.

THE SOUTHEAST MICHIGAN CLEAN AIR COALITION

Another offspring of that conference has been the creation of "The Clean Air Coalition of Southeast Michigan," a coalition consisting of the Michigan DNR, the Southeast Michigan Council of (local) Governments (SEMCOG), the City of Detroit, the counties of Oakland, Wayne and Macomb, and various local businesses, including auto and oil companies and public utilities.

This coalition was conceived by and in no small part executed by GM environmental engineers, two of whom were team members of the EDF/GM dialogue. At stake was the re-designation of Detroit and Southeast Michigan as an attainment area, and an estimated economic stimulus of \$55 million per year to Detroit area industry in avoided EPA compliance costs—a veritable win-win for greater Detroit's environment and for its economy.

In announcing its plans for "Ozone Action! days," the Clean Air Coalition of Southeast Michigan noted at the outset June 1994:

Now that Southeast Michigan has achieved healthy air, our challenge is working to maintain healthy air. One [program] that has been successful in other attainment cities is citizens and businesses in the region taking extra precautions against ozone pollution on days when the region is particularly vulnerable to exceeding the standard (Ozone Action! days). The target days are a result of specific weather conditions—usually hot, sunny days when the temperature exceeds 90 degrees and there is little wind [2].

The coalition urged businesses to modify emission-producing operations on Ozone Action! days, and to make certain that their business vehicles were refueled on non-action days, preferably with less-polluting low-vapor-pressure gasoline where possible. Individuals were urged, among other things, to refrain from cutting their lawns with gasoline powered-mowers, which create as much pollution in one hour as does a new car in 11.5 hours, by not letting automobiles idle for more than a minute; by using car pools and public transportation, by driving their newest, least polluting cars, and, by refueling whenever possible with the lower vapor pressure gasoline, which was supplied by the Marathon Oil Company at no extra cost to consumers.

For its part, the Michigan DNR promised to award partial emissions reduction credits to manufacturers who were able to reduce emissions as a result of this program. The credits would be applicable in any future emissions trading program that the DNR might implement for our area. In addition, area meteorologists and other atmospheric scientists

provided the Coalition with their best weather and ozone forecasts and the local print and broadcast media pitched in to provide frequent ozone advisories.

On February 9, 1995, the program, which had been heavily promoted by Michigan's Governor Engler and Detroit's Mayor Archer, earned Detroit a re-designation as an ozone-attainment area, making it the nation's largest clean-air metropolitan area. Of course, this re-designation can be withdrawn whenever area pollution levels exceed the air quality standards. Accordingly, the program will be an ongoing, continuous effort to maintain Detroit and the surrounding seven-county area as a locus of clean and healthy air as well as a locus of renewed economic growth and vitality. More importantly, the partnership showed how a well-defined cooperative program can bring to bear the efforts of many businesses and more than 1 million households to work for win-win solutions to environmental challenges. As the *Detroit Free Press* pointed out in an editorial in the fall of 1994, the program "not only contributed to our ability to meet air quality standards, but also proved that you can alter people's behavior for clean air and the common good without great pain or inconvenience" [3]. Since that time, a number of other cities have made inquiries regarding the program. In November 1994 the Clean Air Coalition sponsored a workshop to share its experiences with other cities.

THE MAJOR CHALLENGES: DESIGN FLAWS IN THE TRADITIONAL REGULATORY PARADIGM

While environmental partnerships promise significant rewards, there are a number of challenges to be addressed if long-term success is to be assured. Foremost among them is the traditional adversarial nature of environmental policy deliberations, with which so many of us in business, government and the environmental community are all too familiar. All too often, instead of working together to find common solutions, we tend to think and speak in terms of "us" versus "them" and "win" versus "lose."

This counterproductive tension is directly attributable to two fundamental design flaws in traditional command and control regulation. Such regulations are inherently adverse to both *continuous innovation* and *verifiability*—the twin themes of our joint ventures with CERES and EDF. Under command and control regulations, there is no reward for designing greener products or production processes. The only reward is a more expensive or less utilitarian product that leads to unhappy customers and loss of competitiveness in the marketplace. Worse, such regulations tend to punish those who go beyond compliance with best available control technology, by imposing still more stringent and onerous standards. They pit manufacturer against regulator and both against the public interest in a cleaner environment.

Traditional regulations also reduce verifiability as businesses and regulators focus their time and talents on compliance at the expense of performance. Businesses find much of their engineers' time is spent determining and demonstrating why the latest regulatory proposal will not work. Meanwhile, under the command and control paradigm regulators are encouraged to push for further compliance technologies whether or not they achieve measurable emissions reductions. Instead of fostering a process in which both parties work together to further their mutual knowledge of what works and what doesn't, tradi-

tional regulations promote a vicious cycle of "Yes you can!—No I can't!" Consider the historic piecemeal regulation of motor vehicle emissions. Until recently, the approach was not to consider the vehicle as a whole, but to measure emissions only at the tailpipe. And then on a test cycle that could only approximate auto emissions under real world driving conditions, and without considering the type of fuel consumed. While there have been very substantial reductions in tailpipe emissions, we could have achieved still greater environmental benefits at lower overall cost, had not regulatory compliance required us to devote practically all our engineering resources to meeting the requirements of the law—had we had the freedom and flexibility to apply our limited resources to those areas where we might get the biggest environmental bang for the buck.

POWER ENRICHMENT AND THE EPA DRIVING CYCLE

For example, industry engineers have long known that while power enrichment is necessary for performance as well as protection of the engine and catalyst from overheating in severe situations, it does result in elevated emissions levels during some types of driving that are not represented in the EPA driving cycle test protocol. To meet the requirements to reduce tailpipe emissions under the EPA driving cycle consumes practically all of our emissions engineering resources. Although greater environmental benefits would surely ensue if some of those resources could focus on the challenge of power enrichment, the law has not allowed that sort of trade off. Further, even if GM had the additional resources to address this challenge, under command and control regulations such efforts would have placed our products at a competitive disadvantage.

In fact, GM engineers have brought this problem to the attention of both federal and California regulators, and they are working with them to help them develop a new test cycle that will improve environmental performance even while affording sufficient protection to the engine and catalyst. But wouldn't it be better to have a set of regulations that automatically reward those companies that seek out and implement cost-effective solutions and who can themselves benefit from those better ideas in the marketplace? Why not have regulations that encourage engineers and designers to consider the entire vehicle—why not promote policies that take into account how, how much, when and where a vehicle is driven?

TEXAS' WINDSHIELD WASHER FLUID REGULATION

Or consider a recent decision by the State of Texas to comply with the requirements of the amendments to the 1990 Clean Air Act. The amendments put a burden on the states to take corrective actions to bring their non-compliance areas into compliance. Each state has some discretion among the regulation of mobile, stationary and area sources. One of the area sources is windshield washer fluids, whose active ingredient is methanol, a volatile organic compound, which contributes to ozone formation in conditions where direct sunlight can cause chemical reactions with other compounds to form photochemical smog, usually in the summer. These fluids typically contain more than 50% alcohol content in order to ensure maximum protection against windshield ice-up during freezing rain and snow.

Windshield washer fluid is primarily used in the winter, when alcohol emissions usually do not pose an air quality problem. But the EPA's command and control accounting system treats a *ton* of hydrocarbons as a *ton* of hydrocarbons, regardless of the potential to contribute to pollution. The result provides a case study of what can happen when regulations are based on an arbitrary, non-verifiable accounting system.

Under pressure from the federal EPA to reduce hydrocarbon emissions, state air quality regulators have mandated that motor vehicle windshield washer fluids purchased in that state contain no more than 23% methanol content. There are two rather severe problems with this approach. First, since windshield washer fluid is primarily used in the winter, the regulation does little to address the summer time environmental problem. Second, 23% alcohol content is well below the level required to prevent the fluid from freezing in sub-zero weather. While at the request of the auto manufacturers Texas did agree to raise allowed alcohol concentrations from its originally proposed 18 percent level to 23 percent, this level still affords little protection in the sub-zero weather that sometimes characterizes the Texas panhandle region and other regions where Texans may be operating their vehicles.

Texas, laboring under the restrictive rules of the SIP process, and under the watchful eye of the EPA, which is also subject to the same inflexible, arbitrary accounting rules, rejected all other auto industry suggestions, including one that proposed regulating alcohol content only during the warmer months when it poses a realistic threat to the environment. Since ozone formation is mainly limited to the warmer months of the year and in no case occurs under conditions of freezing rain or snow, such a compromise could have achieved the required environmental protection without threatening highway safety.

In our view, a more realistic regulation, one that *fully* considered all the options for reducing mobile source emissions, would have confined the regulation to those regions of the state that face the warmest climates and to those times of year when wintry driving conditions do not create a potential safety problem. By failing to assess any risk-risk tradeoffs—by sticking to the Clean Air Act's command and control requirements for SIP compliance—Texas unwittingly may have increased winter driving hazards for Texas drivers in exchange for little or no benefit to the environment. While the rule does make a contribution to compliance with the accounting procedures required under the Texas State Implementation Plan, such procedures overstate any actual reduction in photochemical smog, since they assume that reductions in volatile organic compounds are equally effective, regardless of the time of year.

CALIFORNIA'S LEV PROGRAM

Consider one final example. According to a study by the California research firm, Sierra Research, headed by Tom Austin, a former CARB official, the incremental cost per ton of the California LEV program ranges from \$18,000 for the so-called "low-emissions vehicle," or to over \$500,000 per ton for the so-called zero emissions vehicle, or ZEV. (The study was funded by the American Automobile Manufacturers Association.) Yet, that same study, as well as a separate study funded by the petroleum industry, estimates that the benefits of the ZEV will be negative! That's because the

incremental cost per vehicle will lead to increased retention of existing higher polluting cars on the road. Austin, in particular, estimates that by 2010 hydrocarbons would be 2% higher than without such a mandate.

There's a better, much cheaper way of achieving these reductions. A program of remote sensing and targeted inspection and repair could achieve a nearly 50% reduction in pollution at an estimated cost of just \$4,000 to \$9,000 per ton. Why such a large reduction at such a low cost? Because the gross polluters, while constituting 10% of the vehicles on the road, account for as much as 50% of California's automotive hydrocarbon emissions.

Asks Patrick Bedard, in a recent issue of *Car and Driver*, "So why, then, do the regulators insist on targeting where emissions aren't, instead of where they are?" In part, he concludes, because of the "necessary rigidity of a command-and-control system. The EPA has an official computer model, and every state and municipality is required to use this model to demonstrate the effectiveness of its air-quality programs.... These models show auto emissions increasing with each year of age, which is true on average, but averages tell the wrong story in a skewed sample" "So we end up in a situation," says Donald Stedman [the pioneer of remote sensing technology,] in which states can't get credit from the EPA for fixing gross polluters because they don't exist in the computer model." [4]

MEETING THE CHALLENGES WILL REQUIRE A MARKET-BASED PARADIGM

In the final analysis, the problem with the EPA driving cycle, the Texas windshield washer fluid regulation, and the California LEV program should not be attributed to either overzealous regulators or, depending on one's point of view, obstructionist business people. Rather, it is endemic to a regulatory paradigm that discourages businesses from seeking out all available strategies and technologies, that punishes their efforts to go beyond what's required, and that encourages business managers and government regulators alike to focus on paper "compliance" rather than real-world performance.

I do not contend that economic incentives alone can solve these design flaws in the command and control paradigm. If a market-based system targets too narrowly just one solution (usually the wrong one), or if phony, "paper" trades substitute for real emissions reductions, a market-based program can be just as destructive as any environmental mandate. There must be clearly defined rules of the game. Regulators must specify the rules of any such programs, including what emissions are to be reduced and what aggregate reductions are to be achieved. They must design monitoring programs that assure performance is accurately measured. They must impose serious penalties for fraud.

But, unlike command and control regulations, properly designed market-based regulations can encourage businesses and regulators alike to seek out and deploy the lowest cost means of achieving emissions reductions. They can turn the creative energies of both businesses and regulators from "why" or "why not" to a search for "what" and "how to." Rather than relying on a few governmental engineers to determine what each business should do—and relying on a few more business engineers to show why their companies can not do it, technical experts everywhere are

invited to test their ideas in the marketplace for improving air quality. Under market-based regulations, verifiable, real performance becomes the objective of everyone because everyone benefits from an improved environment.

Consider GM's experience with so-called mobile emissions bubbles. Since the implementation of the 1977 Clean Air Act Amendments, manufacturers of heavy duty diesel truck engines have been able to average, bank and trade emission reduction credits for particulates. The program has a built-in environmental benefit: 20 percent of any banked tons must be credited to the environment. In 1990 alone, the flexibility afforded by that program encouraged GM powertrain engineers to bank some 307 metric tons beyond the baseline. GM was able to use some of the credits produced by new-generation 1992 and 1993 model year engines to facilitate the continued production of some existing lines.

The ability to average and bank particulate credits has not only led to near-term, concrete environmental benefits (in fact none of the 307 metric tons banked in 1990 was ever used), it also has facilitated environmental innovation. The engineers have been encouraged to make a number of small, but continuous technological improvements that have achieved steady reductions even while reducing the cost of compliance. Finally, the emissions averaging program has enabled the engineers to increase the competitive appeal of the product. In this case, business/government cooperation has created this simultaneous "win" for the environment and "win" for GM and its customers largely because the emissions reductions were market-driven—because the environmental policies created market-driven demands for cleaner air and greener technology.

CONCLUSION

In conclusion, environmental partnerships like the CERES/GM and EDF/GM dialogues, and like Detroit's public-private Clean Air Coalition offer substantial opportunities to promote measurable, verifiable environmental performance and continuous environmental innovation. They show what can be done when "win-win" and "how-to" replace "win-lose" and "yes-no." Ultimately, however, our success will require not just good will and good intentions, but, also a new regulatory paradigm—a paradigm in which environmental and economic performance can go hand in hand. In which, to paraphrase Adam Smith, the private interests of businesses, consumers and regulators alike reflect the public interest in a cleaner environment.

LITERATURE CITED

1. Dudek, Daniel J., Joseph Goffman, Dean A. Drake, and Tom Walton, "Mobile Emissions Reduction Crediting: A Clean Air Act Economic Incentive Policy for Retiring High-Emitting Vehicles." (Environmental Defense Fund and General Motors Corporation, 1994).
2. Clean Air Coalition of Southeast Michigan, "Voluntary Ozone Reduction Program of the Clean Air Coalition of Southeast Michigan," undated press release (June, 1994).
3. *Detroit Free Press* editorial board, "Clean-Air Area: Detroit Met Its Goals: It Deserves New Designation," *Detroit Free Press*, November 12, 1994.
4. Bedard, Patrick, "Still Smoggy After All These Years," *Car and Driver*, 40, (10), p. 115 (April, 1995).

Microbial Sweetening of Sour Natural Gas Using Mixed Cultures

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About twenty-five percent of natural gas produced in the United States is sour containing significant volumes of hydrogen sulfide. Liquid redox processes remove hydrogen sulfide from natural gas. Aqueous solution of chelated ferric ions oxidize the hydrogen sulfide to elemental sulfur. The reduced iron chelate is then oxidized by contact with air and recycled. This requires expensive equipment for regeneration and the process is usually energy intensive.

A microbial process for regeneration of chelated ferric ions may offer an economical alternative to commercial liquid redox processes. The present study investigates the use of a mixed culture of iron oxidizing bacteria to regenerate commercial iron chelate catalysts. The objective of this study is to quantify an increase in the biologically enhanced redox solution reoxidation rates. It was observed that the presence of bacterial cultures enhance the reoxidation rates and sulfur removal significantly. The proprietary mixed cultures of iron oxidizing bacteria used in this study derive the energy required for their growth from the oxidation of reduced sulfur compounds and from the oxidation of Fe(II) to Fe(III) ions in presence of air.

A series of experiments were conducted with a commercial chelated iron catalyst at a constant pH of 7.5 using a total iron concentration of 1000 ppm in the solution. Regeneration of the solution was carried out by passing air through the solution. Sulfur produced was removed by centrifuging in the case of baseline experiments and by vacuum filtration in the presence of bacteria. A 50 to 125% increase was observed in the regeneration rates whereas sulfur yields were 80 to 100% of theoretical in the presence of bacteria as compared to 35 to 50% in the absence of bacteria. Iron oxidizing bacteria were used at cell densities of 1.5×10^9 cells/l to be effective. The pH of the redox solution was observed to be a key process parameter. Other parameters such as temperature, total iron concentration, gas to liquid ratio and bacterial cell densities also influence the overall process.

INTRODUCTION

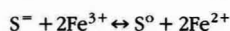
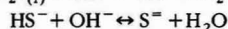
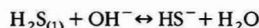
The natural gas industry has long been interested in sulfur recovery technology for applications to streams resulting from treatment of sour natural gas resources [1]. About 14% of U.S. natural gas reserves contain hydrogen sulfide

(H₂S) and other contaminants (2). The sour gas is very hazardous to human health and could cause extensive damage to natural gas pipelines if not properly processed [3]. In order to reduce its health and environmental hazards, and meet the pipeline industry specifications, the H₂S concentrations in natural gas are reduced to less than 4 ppmv. About twenty-five percent of natural gas produced in the United States is sour containing significant volumes of H₂S and other sulfur compounds. The traditional technique for treating this sour gas involves a two-step approach of first separating the acidic gases from the natural gas with an amine plant and then either flaring the hydrogen sulfide or recovering the sulfur in a Claus plant [4]. The liquid redox processes are preferred over traditional Amine-Claus systems because of their simplicity, higher sulfur recovery and good turn down ratio. Scavenger processes are preferred for natural gas streams where sulfur recovery is not economical [5].

The Liquid Redox Sulfur Recovery Processes absorb hydrogen sulfide from the sour gas stream and produce elemental sulfur. The liquid redox processes may use vanadium, iron or a mixture of iron and quinone as the primary catalysts interacting with hydrogen sulfide. The iron-based processes have been most successful because of their superior performance, simple operation, greater reliability and environmental acceptability [6]. However, the process conditions promote the oxidation reactions that accelerate the decomposition of metal-chelate catalysts resulting in high processing costs, and recirculation power requirements. Moreover, in all the commercial liquid redox processes, expensive redox solution is lost via salt formation and inadequate washing of the sulfur cake produced [7].

Redox Process Chemistry

The iron-based redox processes employ iron in the ferric state (Fe³⁺) to oxidize hydrogen sulfide to the elemental sulfur (S⁰). The ferric ion is reduced to the ferrous state (Fe²⁺), which is then regenerated to the ferric state by oxidation with air as follows:



Typical iron concentrations in the chelated catalysts range from 500 to 2500 ppm as determined by economics involving pumping and chemical costs. The LO-CAT chelated catalysts can handle concentrations of H_2S as high as 100% and there appears to be no lower limits [9].

Neither ferrous nor ferric ions are stable in aqueous solutions at neutral or alkaline pH levels and ordinarily will precipitate either as ferrous or ferric hydroxide. This precipitation is prevented by complexing the iron with organic chelates which are capable of holding both forms of iron in solution. These organic chelates are classified into two groups: Type A chelates such as ethylenediamine tetraacetic acid (EDTA) or nitrilotriacetic acid (NTA) which are powerful chelating agents at low pH's; and the type B chelates, consisting of polyhydroxylated sugars that are effective at pH above 8. Combination of both types of chelates makes the catalyst stable at any pH from 5 to 9.0.

The selection of a chelant is dependent on the reaction rate of Fe^{3+} -chelate with H_2S , Fe^{3+} -chelate with oxygen and the rate of degradation of the chelate. The chelate degradation occurs through the oxidation of the chelate by Fe^{3+} ion and the free radical induced oxidation [8]. Other variables that control the oxidative degradation are: pH, chelant concentration, chelant to iron ratio, and the type of degradation products formed.

The LO-CATTM process was originally developed by ARI Technologies, now Wheelabrator Clean Air Systems, Inc., to treat sour gas in the absorber at feed gas pressure and relatively low iron concentrations (1000 to 1500 ppmw) and high circulation rates. This system referred to as conventional LO-CAT works well for many low-pressure plants, however, it results in excessive equipment and pumping costs for high pressure applications. The ARI-LO-CAT II process as shown in Figure 1, was developed for the high pressure direct treat applications [9]. The process uses substoichiometric iron chelated catalyst in the absorber and an oxidizer unit that circulates liquid through density differences. The process is described in greater detail in the literature [9, 10]. The process also uses a separate sulfur settler vessel. These features reduce the chemical and operating costs.

The iron-oxidizing bacteria are capable of oxidizing ferrous ions to the ferric state at low pH. According to the literature references these microbes are capable of oxidizing Fe^{2+} to Fe^{3+} state at 500,000 times faster rate than the purely chemical oxidation process in the absence of bacteria [11]. The regeneration of Fe^{3+} chelate in the presence of acidophilic microbes under mild conditions at 25–45°C, and atmospheric pressure would minimize the chelate degradation process and thus help in improving the economics of hydrogen sulfide oxidation in the natural gas sweetening process. The Fe^{3+} -chelates are also capable of oxidizing the mercaptans to the insoluble disulfides [12]. It is proposed to use these microbes for achieving enhanced ferric ion reoxidation rates in ARI-LO-CAT II process thereby improving the overall sour gas processing economics.

The basic objective of this study, jointly sponsored by U.S. Department of Energy and Gas Research Institute, is to develop information and technology to improve the economics of the commercial iron-based redox processes such as ARI-LO-CAT II and SulFerox, with emphasis on the biologically-enhanced reoxidation of the redox solution used in these processes. In this study, a mixed culture of

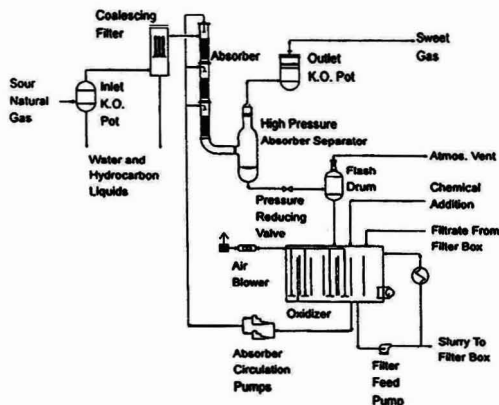


FIGURE 1 Process Flow Diagram for the ARI-LO-CAT II System.

iron oxidizing bacteria were used to regenerate the commercially used iron chelates for reoxidation of reduced redox solutions. There are more than forty gas processing units nationwide using liquid redox technology. These gas processing plants could use the new technology being developed in this project and thus lower the gas processing costs of sub-quality sour natural gas substantially.

MECHANISM OF MICROBIAL OXIDATION OF FERROUS IRON

The iron oxidizing bacteria derive the energy required for their growth from the oxidation of reduced sulfur compounds and from the oxidation of Fe^{2+} to Fe^{3+} ions, using air as an oxidant. The major electron transfer components of the respiratory chain of the iron oxidizing bacteria have been postulated by Ingledew et al. [13] and Cox et al. [14]. These components are organized in the cytoplasmic membrane in such a way as to couple Fe^{2+} oxidation to generate a transmembrane proton electrochemical potential. This potential is the main driving force for electron transfer. A diagrammatic representation of electron transfer mechanism is shown in Figure 2. The major electron transfer components of the respiratory system of the bacteria are comprised of: a cytochrome oxidase, cytochrome c, cytochrome a and a blue colored copper protein, rusticyanin [15]. Ferrous ion oxidation takes place at the cell wall and generates a transmembrane electrochemical potential of 250 mV. The reduction of molecular oxygen is catalyzed by a cytochrome oxidase at a pH of 6.5 on the inside of the cytoplasmic membrane [16].

Components of the iron oxidase are identified by their prosthetic groups and are arranged from left to right in order of increasing redox potential (Cobley and Haddock, 1975; Ingledew and Cobley, 1980). "Out" and "in" refer to the bulk phase and cytoplasm, respectively.

MATERIALS AND METHODS

a. Growth Characteristic of Iron Oxidizing Bacteria

The proprietary iron oxidizing bacteria used in this study were maintained in basal salt solutions at a low pH prior to their use in these experiments. One bacteria (Bacteria A)

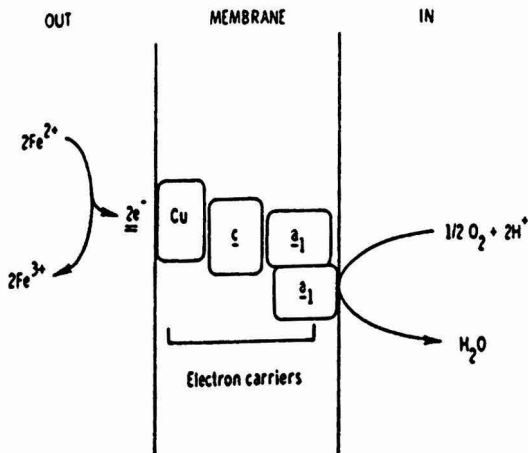


FIGURE 2 Components of the iron oxidase are identified by their prosthetic groups and are arranged from left to right in order of increasing redox potential (Cobley and Haddock, 1975; Ingledew and Cobley, 1980). "Out" and "In" refer to the bulk phase cytoplasm, respectively.

was grown in 9K media and the other bacteria (Bacteria B) was grown in a high pH nutrient media. These bacteria were also grown in a redox solution system for three to five days prior to use in a high pH media maintained at 25° to 45°C in a controlled temperature shaker bath. The composition of nutrient media is shown in Table 1. The iron oxidizing bacterial mixed cultures used in this study were initially obtained from American Type Culture Collection (ATCC), however, they were cultivated either in a high pH media or grown in the redox solution used for the hydrogen sulfide oxidation studies. The cultures were grown separately and then mixed and also were grown in the same media. The maximum cell growth typically occurred in 25 to 50 hours resulting in a cell density of 1.5×10^{11} cells/l in high pH media. The cell densities of 1.0 to 2.0×10^{11} cells/l were achieved in the redox system solutions. Cell densities of $(1.0-1.5) \times 10^9$ cells/l were used in the experiments carried out in the presence of the bacteria. Bacterial cell counts were determined using a Petroff-Hauser bacteria counter under a phase contrast microscope.

b. Gas Samples and Chemical

Synthetic sour gas samples used in this study were blended by Alphagaz Inc. of LaPorte, Texas. The synthetic sour gas had the following composition:

- H₂S - 0.5 (v/v)
- CO₂ - 5% (v/v)
- N₂ - 94.5%

Two types of commercial catalysts, Catalyst A and Catalyst B, were used in this study. These catalysts contain chelated ferric ion complexes. Precipitation of ferric hydroxide is prevented by chelating the ferric ions with organic chelates. Two types of chelates: type A, such as eth-

TABLE 1 High pH Medium for Iron Oxidizing Bacteria

Composition per liter:	
Na ₂ S ₂ O ₃ · 5H ₂ O.....	10.0g
Na ₂ HPO ₄ · 7H ₂ O.....	7.9g
Sodium formate.....	6.8g
Glucose.....	3.6g
KH ₂ PO ₄	1.5g
NH ₄ Cl.....	0.3g
MgSO ₄ · 7H ₂ O.....	0.1g
Trace metals solution.....	5.0mL
pH 7.6-8.5 at 25°C	

ylene diaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA) and type B, such as polyhydroxylated sugars keep the catalyst stable at any pH and were used in the commercial chelated catalyst formulations. This paper presents data using catalyst A only. All other chemicals used were obtained from Sigma Chemical Company.

c. Experimental Procedure

The oxidation of hydrogen sulfide present in the synthetic sour gas blend was studied in a two-liter Virtis Omni Culture Bioreactor shown in Figure 3 [17, 18]. The hydrogen sulfide is readily oxidized by the chelated ferric ions present in the commercial catalyst A used in this study. The ferric ions (Fe³⁺) are reduced to the ferrous state (Fe²⁺) and hydrogen sulfide is oxidized to elemental sulfur. The elemental sulfur is removed by filtration or centrifuging and the ferric ion is regenerated by bubbling air through the reduced redox solution under controlled experimental conditions. The rate of hydrogen sulfide oxidation is a function of the pH, temperature, concentration of Fe³⁺ chelate, the gas/liquid ratio and the degree of agitation. These variables were carefully controlled and optimized. Likewise, the rate of ferric ion regeneration is a function of the pH of the redox solution, the temperature, the concentration of chelated iron, air to redox solution ratio and the degree of agitation. The progress of the reaction was monitored by measuring the concentration of Fe²⁺, Fe³⁺, pH, temperature, and redox potential of the reaction medium in the

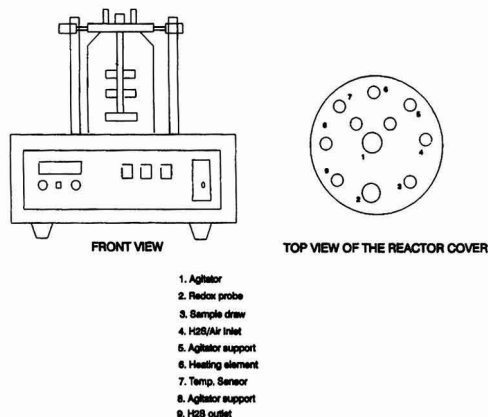


FIGURE 3 Omni culture bio-reactor.

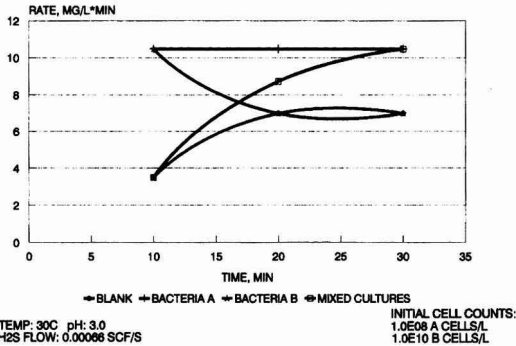


FIGURE 4 Comparison of H₂S oxidation rates with and without bacteria.

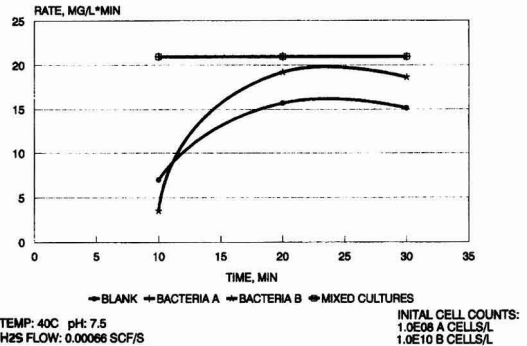


FIGURE 6 Comparison of H₂S oxidation rates with and without bacteria.

Virtis Omni Culture Bioreactor. Two sets of experiments were conducted in each case, one in absence of bacteria (blank) and the other one in presence of a single bacteria or a mixed culture.

1. One-Cycle Experiments Using Commercial Chelated Catalysts. (Absence of Bacteria)—Baseline

A set of experiments was conducted at 30°C to 45°C and a pH varying from 3, 5 and 7.6 using 1000 ppm solution of commercial iron-chelate Catalyst A in absence of iron oxidizing bacteria (baseline). A cycle consists of oxidation of hydrogen sulfide by bubbling it through redox solution, filtration of elemental sulfur followed by reoxidation of ferrous ions with air. In a typical experiment, hydrogen sulfide was oxidized by passing the synthetic sour gas mixture through one liter of redox solution in Virtis Omni-Culture Bioreactor, elemental sulfur was centrifuged after each cycle and the redox solution was regenerated by bubbling air through it in absence of bacterial cells (blank run). The data on these experiments is shown in Figures 4 to 6. The redox solution regeneration rates were fairly constant, for a specific pH, temperature and gas to liquid ratio in the control (baseline) experiments and the quantity of elemental sulfur recovered ranged from 35 to 50% of the theoretical amount.

2. One Cycle Experiments Using Commercial Chelated Catalyst A in Presence of Iron Oxidizing Bacteria

In this set of one-cycle experiments the iron oxidizing bacterial cells of bacteria A, B or a mixed culture were used in the redox solution containing 1000 ppm of commercial chelated Catalyst A at 30°C to 45°C and a pH of 3.0 or 7.5. In a typical experiment, hydrogen sulfide was oxidized by bubbling the synthetic sour gas mixture through one liter of redox solution contained in the Virtis Omni-Bioreactor, elemental sulfur produced was filtered (not centrifuged) after each cycle and the redox solution was regenerated by bubbling air through the solution containing iron oxidizing bacteria or a mixed culture at a cell concentration of $1 \text{ to } 7.5 \times 10^9$ cells/liter. The data are presented in Figures 4, 5 and 6 and compared with the baseline experimental data obtained in absence of bacteria. The data show a ferric ion regeneration rate enhancement of 50 to 150% and an increased production of elemental sulfur, 80 to 98% recovery as compared to 35 to 50% recovery in absence of bacteria. The data on rate enhancement is shown in Figures 7 and 8 and the data on sulfur recovery is given in Figures 9 and 10.

DISCUSSION OF RESULTS

The oxidation of hydrogen sulfide present in the synthetic sour gas mixture blended by Alpagaz of LaPorte,

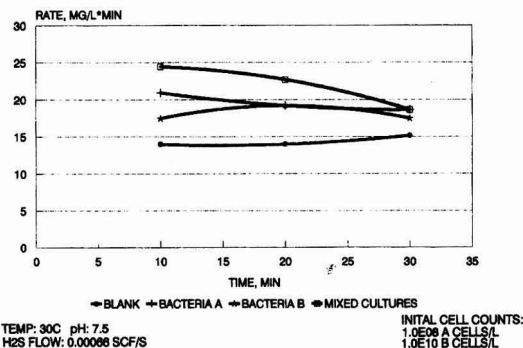


FIGURE 5 Comparison of H₂S oxidation rates with and without bacteria.

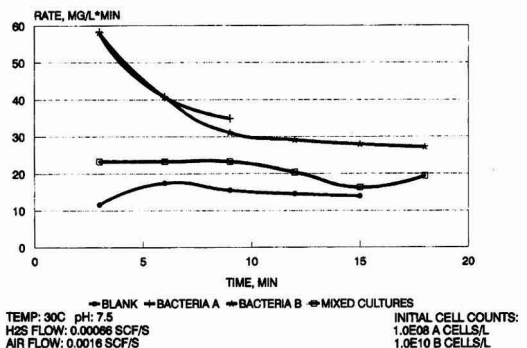


FIGURE 7 Comparison of regeneration rates with and without bacteria.

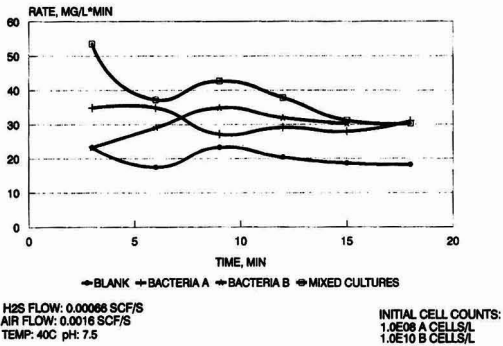


FIGURE 8 Comparison of regeneration rates with and without bacteria.

Texas has been studied using a commercial chelated iron catalyst in a two-liter Virtis Omni-Culture Bioreactor. The rate of hydrogen sulfide oxidation was found to be primarily influenced by the pH, temperature, gas/liquid ratio and the concentration of iron chelate in the redox solution. Essentially all hydrogen sulfide was oxidized to elemental sulfur in the presence of commercial iron-chelate catalysts at a pH of 7.5 and 30 to 45°C. There was a 20% rate enhancement in hydrogen sulfide oxidation in the presence of mixed cultures.

The regeneration of the ferric ions in the chelated catalysts could be accomplished by bubbling air through the reduced chelated catalyst in the bioreactor. The air regeneration of the chelated ferric ions was dependent on the pH, temperature, air/redox solution ratio and the bacterial cell concentration. Single cycle experiments were carried out both in absence of iron oxidizing bacteria (blank), as well in presence of the bacterial cells. The ferric ion regeneration rates in the reduced redox solution were found to be 50% to 150% higher in presence of bacterial cells at typical cell density of 1 to 5×10^9 cells/l under optimum operating conditions. The data are presented in Figures 7 and 8 with a commercial chelated catalyst in one-cycle experiments.

The sulfur recovery was also studied in single cycle experiments. Invariably, 35 to 50% sulfur was recovered by centrifuging in the controlled blank runs, whereas in presence of mixed cultures of iron oxidizing bacteria the sulfur

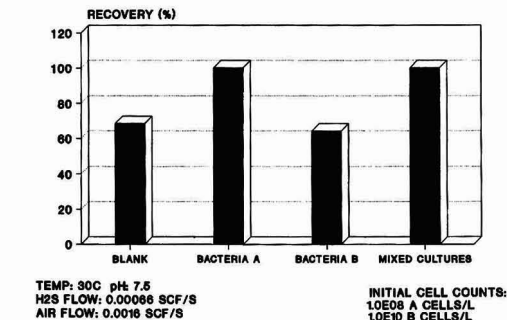


FIGURE 9 Comparison of sulfur recovery with and without bacteria.

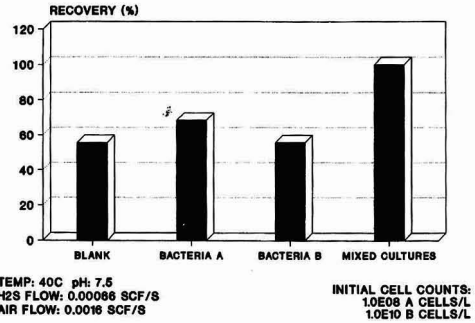


FIGURE 10 Comparison of sulfur recovery with and without bacteria.

recovery ranged from 80 to 100% of the theoretical values. It was observed that filtration was the preferred technique for sulfur recovery in the presence of iron-oxidizing bacteria, since centrifuging affected the bacterial cell densities in the redox system. The sulfur recovery data for one-cycle experiments are shown in Figures 9 and 10.

CONCLUSIONS

One of the bacterial strain (Bacteria A) was readily grown in 9K media and the other iron-oxidizing bacteria (Bacteria B) used in this study was grown in a high pH medium containing trace metals. Cell densities as high as 2×10^{11} cells/l could be achieved in twenty to fifty hours. Moreover, the high pH medium could be easily replaced by the used redox solution of the commercial catalyst evaluated in this study without adversely affecting the growth characteristics and the bacterial cell densities of the iron-oxidizing bacteria and the mixed cultures.

These experiments conclusively show that in the presence of iron oxidizing bacteria, Bacteria A, or B or the mixed cultures, the rates of hydrogen sulfide oxidation are enhanced by about 20%, the ferric ion reoxidation rates in the redox system of the commercial chelated redox catalyst are enhanced by 50% to 150% as compared to blank runs in absence of bacterial cells at an operating pH of 7.5 and the redox solution temperature varying from 30° to 45°C. Moreover, the iron oxidizing bacteria also induce higher elemental sulfur recoveries ranging from 80 to 100% of theoretical as compared to 35 to 50% in absence of bacteria.

ACKNOWLEDGEMENTS

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LITERATURE CITED

1. **Kohl, A., and F. C. Reisenfeld**, *Gas Purification*, Gulf Publishing, Houston, Texas (1979).
2. **Hugman, R. H., E. H. Vidas, and P. S. Springer** (Energy and Environmental Analysis, Inc.), "Chemical Composition of Discovered and Undiscovered Natural Gas in the Lower-48 United States—1993 Update," Volume I. Report No. GRI-93/0456.1.
3. **Leppin, D., and H. S. Meyer**, "Gas Research Institute Program in Natural Gas Processing," Paper SPE 21505 presented at SPE Gas Technology Symposium, Houston, TX (January 1991).
4. **Dalrymple, D. A., T. W. Trofe, and J. M. Evans**, "An Overview of Liquid Redox Sulfur Recovery," *Chemical Engineering Progress*, pp. 43–49 (March 1989).
5. **Quinlan, M. P.**, "Technical and Economic Analysis of the Iron-Based Liquid Redox Processes." Proceedings of the 71st Annual Gas Processors Association Convention, Anaheim, CA (March 1992).
6. **Leppin, D.**, "Update on GRI Sulfur Recovery Research." Proceedings of the 1992 Liquid Redox Sulfur Recovery Conference, Austin, TX (October 1992), GRI Report No. GRI-93/0129.
7. **Leppin, D., J. M. Evans, and K. Krist**, "Gas Research Institute Program in Sulfur Recovery Research." Proceedings of the 1991 Liquid Redox Recovery Conference, Austin, TX (May 1991), GRI Report No. GRI-91/0188.
8. **Kundu, K. P., and N. Maturra**, *Internat. J. Radiation Phys. Chem.*, Vol. 3, 1 (1971).
9. **Hardison, L. C.**, "LO-CAT II—A Big Step Forward in Iron Redox Chemistry." Proceedings of the 1991 Liquid Redox Sulfur Recovery Conference, Austin, TX (May 1991), GRI Report GRI-91/0188.
10. **Hardison, L. C.**, (ARI Systems, Inc.), "Early Experience with ARI-LO-CAT II for Natural Gas Treatment," Presented at AIChE Spring National Meeting, New Orleans, Louisiana (March 29–April 2, 1992).
11. **Lacey, D. T., and F. Lawson**, "Kinetics of Liquid Phase Oxidation of Acid Ferrous Sulfate by the Bacterium *Thiobacillus ferrooxidans*," *Biotechnology and Bioengineering*, xii, pp. 29–50 (1970).
12. **Agumadu, P. N., and C. Rai**, "Microbial Sweetening of Sour Gas," 1991 GRI Liquid Redox Sulfur Recovery Conference, Austin, Texas (May 5–7, 1991), GRI Report No. GRI-91/0188.
13. **Ingledeu, W. J.**, "Ferrous Ion Oxidation by *Thiobacillus ferrooxidans*," *Biotechnology and Bioengineering Symposium* No. 16, p. 23–32 (1986).
14. **Cox, J. C., and M. D. Brand**, "Iron Oxidation and Energy Conservation in Chemoautotroph *Thiobacillus ferrooxidans*," p. 31–46. In W. R. Strohl and O. H. Touvinen (ed.), *Microbial Chemoautotrophy*. Ohio State University Press, Columbus, Ohio (1984).
15. **Rawlings, D. E., and T. Kusano**, "Molecular Genetics of *Thiobacillus ferrooxidans*," *Microbiological Reviews*, **58** (1), p. 39–55 (March 1994).
16. **Rai, C., and J. Rao**, "Biologically-Enhanced Redox Solution Reoxidation." Proceedings of the GRI 1994 Sulfur Recovery Conference, Austin, Texas, p. 199–214 (May 15–17, 1994).
17. **Gokarn, R. R.**, "Process Optimization for Microbial Sweetening of Sour Natural Gas." M.S. Thesis, Texas A&I University, Kingsville, TX (August 1993).
18. **Dinesh-Mohan, H. K.**, A Novel Microbial Sweetening Process for Sour Natural Gas Upgrading. M.S. Thesis, Texas A&I University, Kingsville, TX (1992).
19. **Rai, C.**, "Microbial Desulfurization of Coals in a Slurry Pipeline Reactor Using *Thiobacillus ferrooxidans*," *Biotechnology Progress*, **1**, 200–205 (1985).
20. **Satoh, H., J. Yoshizawa, and S. Kametani**, "Bacteria Help Desulfurize Gas." *Hydrocarbon Processing*, pp. 76-D to 76-F (May 1988).
21. **Leppin, D.** (Gas Research Institute), "GRI Program in Sulfur Removal and Recovery from Natural Gas—1994 Update," Presented at GRI Sixth Sulfur Recovery Conference, Austin, Texas (May 15–17, 1994).

Preparation and Evaluation of Adsorbents from Waste Carbonaceous Materials for SO_x and NO_x Removal

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This paper presents studies of a new integrated process for simultaneous SO_x and NO_x removal and utilization of waste carbonaceous materials. It is mainly centered on some fundamental aspects of preparing microporous adsorbents from solid wastes such as coal reject, sewage sludge and sawdust. Surface area and pore structural evolution are investigated to illustrate the importance of processing parameters such as pyrolysis temperature and hold time, activation methods and carbon burn-off, etc. It is shown that pyrolysis temperature, activation chemicals used and carbon burn-off have significant effects on the surface area development and pore structure evolution. There exist an optimal pyrolysis temperature and hold time for maximum surface area development for all precursor materials. Physical activation of coal reject char after pyrolysis can improve the surface area of the derived chars, while chemical treatment in ZnCl₂ can enhance the microporosity of sewage sludge char. In physical activation, carbon burn-off or hold time is a critical factor in determining the surface area. Concentration of the activating agent is an important factor in chemical treatment of sewage sludge. Adsorption characteristics of the wastes-derived adsorbents with respect to SO₂, H₂S, and NO_x are also studied in this work. It is shown that solid wastes such as sawdust and coal mining wastes can be converted into effective adsorbents for SO₂ and NO_x removal from flue gases, whilst activated chars derived from sewage sludge have been shown to be promising adsorbents for H₂S removal. The significance of using waste solids is two-fold: on one hand the waste materials are utilized or minimized; on the other, they can replace or partially substitute the expensive activated carbons for the removal of SO_x and NO_x.

AN INTEGRATED PROCESS FOR SO₂ AND NO_x REMOVAL

Facing the stringent regulations on acidic gas emissions such as SO₂ and NO_x, industrial sectors, particularly the power and metal industries have paid much attention to the development of cost effective technologies to control these air pollutants. Generally, research efforts are either to eliminate/reduce SO₂ emissions before and during combustion processes or to remove them from flue gases. These purposes can be accomplished by desulfurization of fuels, reduction of SO₂ formation during combustion and flue gas desulfurization (FGD). While the desulfurization of fuels

plays a limited role in reducing the emission of SO₂, removal of sulfur dioxide both during and post-combustion has drawn a great deal of research attention. For the reduction of NO_x emission there are two basic approaches, one of which is through combustion technologies such as reduction of excess oxygen, staged combustion and flue gas recirculation, etc. to eliminate the formation of nitrogen oxides. These combustion techniques can significantly reduce the emission of NO_x to some level (up to 70–80%), but not sufficient to meet the requirements of pollution standards. Therefore, removal of NO_x from the flue gases is inevitably important in reducing NO_x emission to a satisfactorily low level. Numerous processes have been developed and some of them are commercialized while the improvements of existing technologies and disclosure of new processes are continuing. The processes developed so far can be categorized into two main groups, namely, wet and dry methods. The disadvantages of the wet systems are apparently high capital and operating costs, the formation of nitrate anion materials requiring secondary treatments and production of a great amount of sludge that is also a problem [7]. On the contrary, dry processes are relatively economical due to their simplicity and generally do not produce any secondary waste stream. Dry processes offer distinct advantages over the wet ones and more applicable than the wet one. Dry methods mainly consist of recovery of SO₂ and NO_x by adsorption and reduction or decomposition of NO_x. Numerous studies on SO₂ dry sorption techniques have been done. Although dry methods have drawn much attention of research interests they are by no means accomplished. Each process does have some advantages and is also subject to some drawbacks either technically or economically. A comprehensive review of the various FGD and denitrification processes is available [8].

Based on an evaluation of existing technologies for SO₂ and NO_x removal and examination of adsorption potential of solid waste materials such as fly ash, coal reject and sawdust, etc., we proposed a new process for the removal of these pollutants. The following considerations have been taken into account when designing such a process:

- i) simultaneous removal of SO₂ and NO_x;
- ii) combination of SO₂ sorption and catalytic decomposition of NO_x;
- iii) utilization of solid wastes.

Figure 1 is a schematic diagram showing the proposed process. The process basically involves three-stage simultaneous removal of SO₂ and NO_x from the flue gas stream.

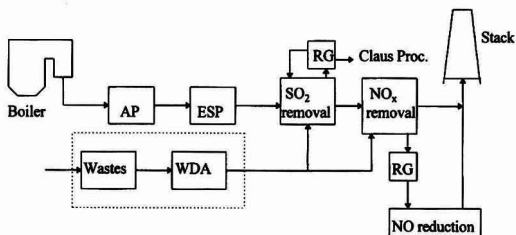
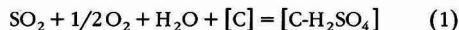


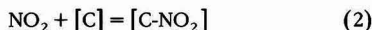
FIGURE 1 Flow scheme for an Integrated SO_2 and NO_x removal (AP—Air preheater, ESP—Electrostatic Precipitator, RG—Regeneration, WDA—Waste Derived Adsorbents).

At stage I, most of the SO_2 in the flue gases will be removed by using waste solid derived sorbents. The spent sorbent can either be regenerated or thrown away. The SO_2 -rich gas after regeneration undergoes a Claus process to produce elemental sulfur or directly to produce sulfuric acid. A main reaction step is [13]:

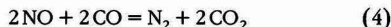
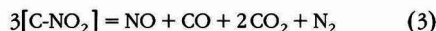


in the temperature range 100°C – 200°C .

After the SO_2 removal stage, the temperature of the flue gas stream is cooled down to around 25 – 50°C . Nitrogen oxide is then mainly NO_2 in this temperature range. Consequently, we can use the waste solid-derived sorbent to concentrate NO_2 by adsorption



The following step is to desorb NO_2 at 200 – 350°C to generate a gas stream of concentrated CO_2 , NO , N_2 , and CO . The concentrated NO produced then can be catalytically reduced in the presence of CO . The basic reactions are



Obviously, the regeneration or desorption of NO_2 consumes carbon. The process would be very expensive if commercial activated carbon were used here. Therefore, waste carbonaceous materials will serve as suitable substitutes. The advantage of this process is that cheap (practically free) waste materials are utilized in a simultaneous SO_2 and NO_x removal system. This can, on the one hand, minimize or replace the use of expensive sorbents like mixed metal oxides and activated carbon and, on the other hand, abate to some extent the solid waste pollution. Furthermore, additional reducing agent, like troublesome gas ammonia, is not used in this process.

SORBENT PREPARATION FROM WASTES

Properties of Waste Carbonaceous Materials

In principle, all sorts of waste carbonaceous materials can be converted to adsorbents with varying surface area and pore structures. Depending on the properties of precursor

material, the quality of resultant adsorbents would be quite different. In a number of projects aiming at producing effective adsorbents for SO_x and NO_x , coal washery reject, sawdust and sewage sludge have been trialed.

Coal reject, a waste product of coal preparation processes, is usually disposed of by damping and landfill. The increasing quantity of coal reject has become a major environmental management issue in Australian coal industries. Sawdust is another carbonaceous waste generated in sawmills. The timber industry in Australia has started to pay more attention to the utilization of wood chipping and processing wastes. Sewage sludge is traditionally landfilled in most countries. In land scarce countries like Singapore, landfill is no longer a viable option. Incineration and sludge-to-oil have been considered as possible alternatives to the sewage sludge disposal. Obviously making adsorbent from sewage sludge is also worthy of experimentation.

Coal reject samples used in this study were obtained from Rhonda Collieries, Ipswich, Queensland, Australia, and the coal type is medium-volatile bituminous [9]. The proximate analysis and physical properties are summarized in Table 1. Sawdust and anaerobically digested sewage sludge were from a local sawmill and Kranji Sewage Works in Singapore, respectively.

It is clear that both coal reject and sewage sludge contain large amounts of ash. The resultant chars from these materials would normally have high ash content. However, the total surface areas of the chars are mostly attributed to their carbon matrix. This was confirmed with a separate experiment whereby the ash after total burning of the carbon was characterized and found to have insignificant surface area [12]. Water analyzed here is basically the pyrolytic water which is liberated from the coal reject upon heating to 200°C since the physically sorbed water was already removed before the analysis. For sawdust, most of the constituents are volatile matters and there are large amounts of water in the sewage sludge even though it was dewatered sludge. The coal reject sample has fairly high specific surface area compared to sawdust.

It is the volatile matter that will be literated during high temperature treatment during which process a rudimentary pore structure is formed in the char. The resulting char can then be activated in an oxidizing atmosphere and the adsorptive capacity of this char is thus improved as result of the surface area enlargement. Fixed carbon contents of these materials are generally very low which indicate a high volume reduction (low yield) and this is favorable because large quantities of wastes can be utilized in this way.

TABLE 1. Physical and Chemical Properties of Carbonaceous Wastes

Properties	Coal reject	Sawdust	Sewage sludge
Water content	2.29%	15.01%	48.75%
Volatile matter	17.81%	67.44%	26.60%
Fixed carbon	10.73%	16.91%	5.74%
Ash	69.17%	0.73%	18.91%
Size range	100–2000 μm	500–710 μm	120–1500 μm
BET surface area	7.14 m^2/g	0.82 m^2/g	4.74 m^2/g
Particle density	2.26 g/cc	1.47 g/cc	1.19 g/cc

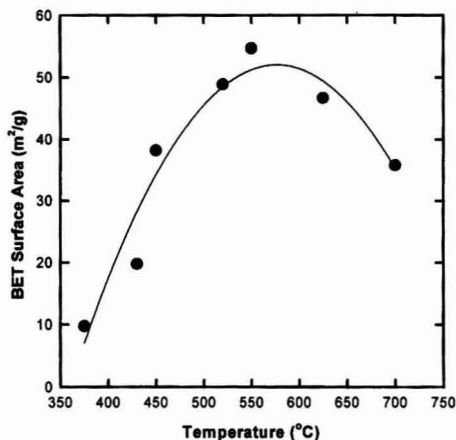


FIGURE 2 Surface area development of coal reject as a function of pyrolysis temperature.

Experimental Techniques

Pyrolysis of waste carbonaceous materials was done in a fixed bed reactor in N_2 at temperature range of 450–900°C and the resulting chars are characterized by ASAP 2000 for surface area and pore size distribution. A Thermogravimetric Analyser (TGA) with a gas mixing and control panel was used for the adsorption experiments. Detailed description of experimental methods can be found elsewhere [8, 12].

Surface Area and Pore Structure Development During Carbonization

Effect of Pyrolysis Temperature

Figure 2 shows that the surface area of the pyrolyzed coal reject char (CRC) increases with temperature, for a given residence time of 2.5 hr, passes through a maximum and then decreases as temperature further increases. This is a general behavior of thermal decomposition, which is also observed by other researchers [5, 14]. This phenomenon can be explained by two effects: the first effect is that new pores are developed as volatile matter is liberated during pyrolysis and hence the accessible microporosity and surface area increase. Second, as the heat treatment temperature is raised, a shrinking of the particle and a narrowing of the pore entrances occur, resulting in a decrease of the accessible micropore surface area [4].

Interestingly, the temperature at which the surface area is maximum is found at about 550°C, which is in the range of 400–600°C. This verifies the theory of crystallite thermal alignment by Walker, Jr. [16]. It is believed that the poor alignment or packing of the building blocks of the precursor during thermal treatment yields the generation of micropores in the carbon matrix. It is in this temperature range of 400–600°C that most organic solids begin to lose hydrogen and produce free-radicals, which are then condensed into larger molecular units and ultimately lead to a microporous texture in the precursor. As a consequence of microporosity increase, a higher internal surface area is acquired.

Figure 3 shows the surface area development of sawdust and sewage sludge with temperature during pyrolysis. For

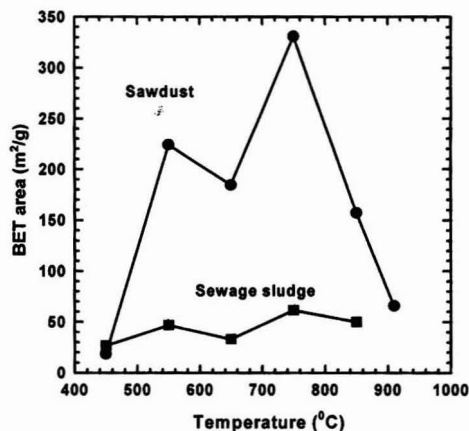


FIGURE 3 Surface area development as a function of carbonization temperature for 3h hold time.

a given hold time of 3 hours, the surface area exhibits quite different trends from that of the coal reject chars. The surface area generally increases with temperature, however, with the exception at about 650°C. At around 650°C, the surface areas of the chars from sewage sludge and sawdust show a dip. This could be explained that in this temperature range, there was intermediate melt formed and secondary volatile evolved. As the intermediate product was softened and gases bubbled out, relative large pores resulted in the final char. This is also demonstrated in Figure 4 showing the pore size distributions for sewage sludge chars obtained at various temperatures for a hold time of 2 hour. The pore structure of the char obtained at 650°C is largely mesoporous and macroporous with an average pore diameter of 12 nm, whereas the chars obtained at higher temperatures are more microporous with mean pore sizes of 5.5–7 nm.

Effect of Heating Rate

Heating rate has been shown to be an important factor in pyrolysis. Heating rate affects not only the pyrolysis re-

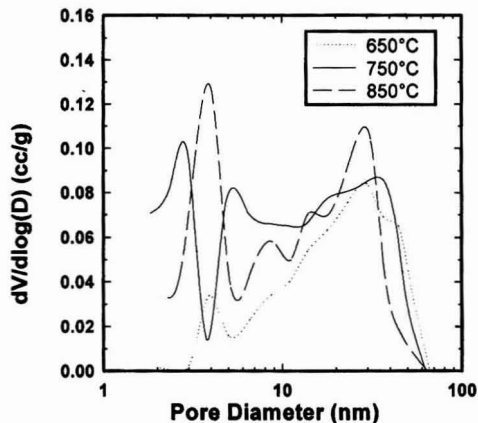


FIGURE 4 Pore size distribution of chars from sludge at different temperatures (2 hr hold).

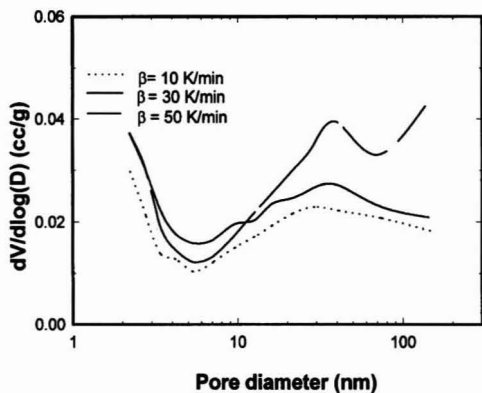


FIGURE 5 Pore volume distributions of coal reject chars pyrolyzed at various heating rates.

action rates but also influences the rate of particle softening and swelling and consequently the pore structure evolution. It has been shown that increasing the rate of heating during pyrolysis of coal enhances the plasticity and thus increases swelling of the particle [10, 15]. In this way, one would expect a decrease in micropore surface area and increases in mesopore and macropore surface areas.

Figure 5 shows that increasing heating rate promotes mesopore generation, revealing that the enhanced softening and swelling at higher heating rates result in the development of large pores due to the abrupt release of trapped volatile in the coal reject particle [10]. The constant micropore volumes for all chars at different heating rates do not necessarily mean that the micropore structure is not affected by heating rate, but it is likely due to the combination of effects of heating rate on softening and shrinking. It is understood that both softening and shrinking can reduce microporosity, but the effects of heating rate on the pore structure evolution are different. At higher heating rates pyrolysis would on one hand generate larger pores due to softening effect. On the other hand, the existing micropores are preserved in the shorter period of shrinking. Therefore, the total micropore volume is seen not to vary with heating rates significantly.

Effect of Hold Time

Hold time is the residence time of the sample in the furnace after the pyrolysis temperature is reached. It is another important process parameter affecting the surface area development. Figure 6 shows that the BET surface area generally increases with hold time, levels off after about 3 hours for all precursor materials. The rate of surface area development is clearly shown in Figure 6. It is seen that the rate in surface area evolution is directly related to the volatile matter content in the precursor material.

Table 2 summarizes the best adsorbent properties obtained by pyrolysis of these waste materials. It is seen that sawdust derived char has the highest surface area simply because it has more volatile and carbon contents. If the surface area is calculated based on unit of carbon present in the char, coal reject char (CRC) has the highest surface area.

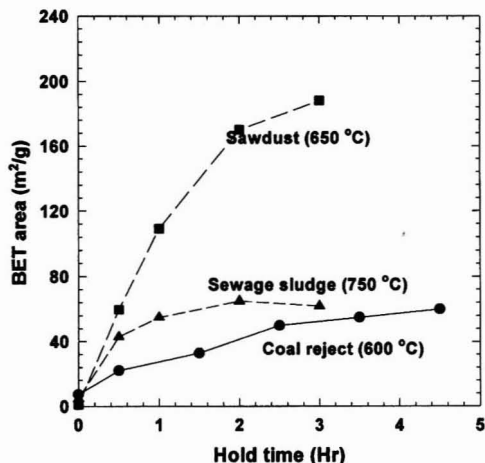


FIGURE 6 Effect of hold time on surface area development during pyrolysis.

Further Improvement on Pore Structure by Activation

Physical Activation

During carbonization process in N_2 , micropores were formed in the carbon matrix but were normally too small to affect the adsorption of gas molecules. Therefore, activation of this char is needed to remove some of the carbon atoms to further enlarge the micropore size as well as to increase the micropore volume. Controlled gasification in oxidative atmosphere is generally used for coal-based materials [1]. In this work, we use CO_2 as an oxidant and activation experiments were performed. It is found that carbon burn-off (or hold time) is critically important in influencing the pore structure of the activated char.

The variation of internal surface area of coal reject char with carbon burn-off is shown in Figure 7. As gasification proceeds, the closed pores are opened and open pores are enlarged, so that the surface area increases sharply. This increases up to a point (see Figure 7) at which the pore walls begin being consumed and the total number of open pores begins to decrease with further activation, and hence the surface area begins to decrease. It is also shown in Figure 7 that the micropore surface area behaves in the same manner as the total surface area. This is because that most of the surface area of the initial CRC is attributed to the micropore surface. Figures 8 is a plot of pore volume distribution as a function of carbon burn-off. We note that the

TABLE 2. Best Adsorbents from Pyrolysis of Waste Materials in N_2

Materials	BET Surface area (m^2/g)	Mean pore size (nm)	Pyrolysis Condition		
			T ($^{\circ}C$)	Time (hr)	Heat Rate (K/min)
Coal reject	60.2	8.4	625	4.0	10.0
Sewage sludge	88.4	5.8	850	2.0	20.0
Sawdust	376.4	3.6	850	2.0	20.0

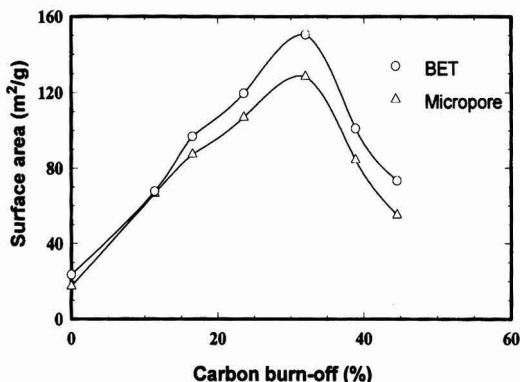


FIGURE 7 Effect of carbon burn-off on the surface area development of CRC activated at 900°C in CO₂.

starting CRC possesses low microporosity. This is because most of micropore in the initial coal reject or pyrolyzed CRC are not accessible to the adsorbate when the surface area is measured. Nevertheless, the pore volume evolution is much similar to that of the total surface area.

Chemical Activation

The surface area of the sawdust char achieved by pyrolysis (376 m²/g) was considered to be very high and adequate for application to SO_x/NO_x removal. Therefore, no experiments were performed on activation of sawdust. Sewage sludge chars resulted from pyrolysis were also subjected to CO₂ activation. It is shown that the control of carbon burn-off was very difficult and consequently the surface area declined dramatically after the physical activation. It was decided this method was not suitable for sewage sludge char. Chemical treatment or activation was used for sewage sludge chars in this study and proven to be effective in improving the surface area and pore structure.

At room temperature, dried sewage sludge was first soaked in various concentrations of Zinc Chloride solu-

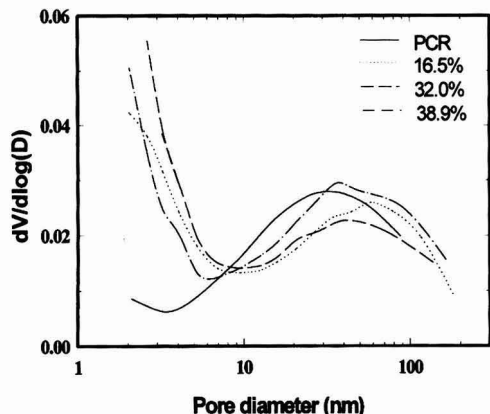


FIGURE 8 Change in pore volume distribution with carbon burn-off during CO₂ activation at 900°C.

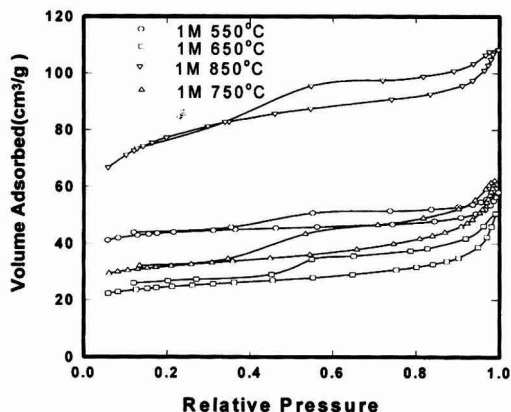


FIGURE 9 Effects of pyrolysis temperature on N₂ adsorption isotherms of ZnCl₂ treated sludge.

tions and then pyrolyzed in N₂ at different temperatures. Figure 9 shows the effect of pyrolysis temperature on the N₂ adsorption isotherms of chars obtained at 850°C and for 2 hr hold time. It is seen that adsorption volume at temperatures below 750°C is much lower than that for 850°C. All these isotherms are of type I suggesting that micropores dominate the pore structure. The char obtained at 850°C for 2 hr has a surface area of 276 m²/g, much higher than that resulted from the sludge without chemical activation [6].

The studies on chemical activation of sewage sludge showed that the concentration of ZnCl₂ is also an important parameter. Figure 10 shows the pore size distributions of chars resulting from pyrolysis of ZnCl₂-treated sewage sludge. The effect of the molar concentration is clearly demonstrated. It is seen that there is an optimal concentration of ZnCl₂ for the activation. Solution of 5 M is found to give the most micropores. The activating agent ZnCl₂ is believed to be a dehydrating agent resulting in inhibition of tar formation during pyrolysis. Thus it enhances the carbon yield and formation of micropores [2]. However, at too high a concentration, the salt crystals may well effectively

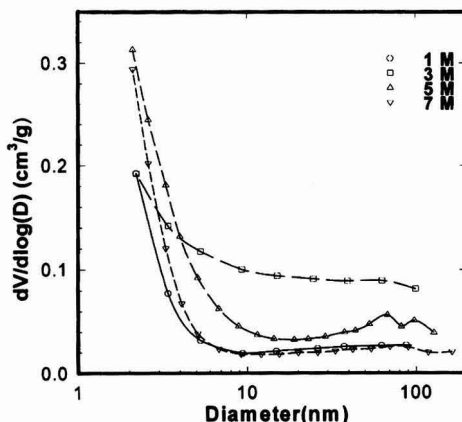


FIGURE 10 Pore size distributions of sewage sludge derived chars activated with various concentrations of ZnCl₂.

TABLE 3. Best Activated Chars Prepared from Coal Reject and Sewage Sludge

Materials	BET Surface area (m ² /g)	Mean pore size (nm)	Activation Condition
Coal	155.2	5.3	Pyrolysis: 600°C, 4 hr, 10 K/min Activation: CO ₂ 900°C, 32% burn-off
Sewage sludge	309.3	3.8	ZnCl ₂ 5 M, T = 650°C, 2 hr, 20 K/min

block some micropores accessible to the adsorbate thus resulting in a decrease in adsorption capacity or surface area. This has been observed in SEM examination of the pyrolyzed chars with high ZnCl₂ concentrations [6]. Table 3 summarizes the best adsorbents derived from coal reject and sewage sludge activation. CRC is shown to have a higher micropore area to BET area ratio.

APPLICATION OF WASTE-DERIVED SORBENTS

To test the adsorption capacity of waste derived adsorbents, experiments were conducted on adsorption of NO₂ and SO₂ on coal reject, sawdust and sewage sludge derived chars at 25°C. A TGA technique is used with a gas mixing system consisting of high resolution flowmeters and pressure regulators. Details of experimental conditions and apparatus are given elsewhere [8, 12].

The adsorption capacities of coal reject chars (based on unit mass of activated CRC sample) of different carbon burn-off CRCs are given in Figure 11. It is seen that a considerable NO₂ adsorption capacity is obtained for most of the CRCs. The CO₂ activation of pyrolyzed char improves the NO₂ adsorption by a factor of 2, whilst the capacity for SO₂ is not significantly increased by activation.

Figure 11 shows that the adsorption capacities of the activated CRCs reach maxima at about 17% carbon burn-off. This occurs before the carbon burn-off point where maximum surface area occurs (see Figure 7). This is because the micropore structure development in early stage of carbon

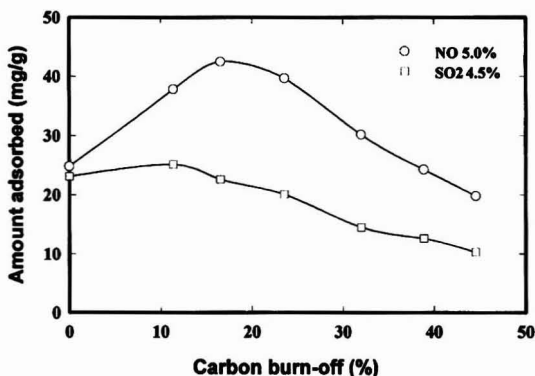


FIGURE 11 Adsorption capacity of CRC for SO₂ and NO₂ at 25°C.

TABLE 4. Adsorption Capacities of Waste Derived Adsorbents at 25°C

Adsorbents	BET surface area (m ² /g)	SO ₂ (4.5%)	NO ₂ (5.0%)
Coal reject	134.4	24.5 mg/g	45.6 mg/g
Sewage sludge	239.3	46.3 mg/g	34.5 mg/g
Sawdust	376.4	178.2 mg/g	234.9 mg/g
Ajax carbon	1200	504.9 mg/g	337.5 mg/g

burn-off stage is more prevalent. It is obvious that the adsorption capacity for an adsorbate is closely related to the micropore surface area of the CRC sorbent.

Table 4 shows the adsorption capacities of SO₂ and NO₂ on the best adsorbents derived from sawdust pyrolysis, coal reject and sewage sludge activation (ZnCl₂) compared to that of commercial activated carbon (Ajax) [3].

It is seen that the adsorption capacity of sawdust derived adsorbent has the highest adsorption capacity for SO₂ and NO₂. Whereas sewage sludge derived char has the lowest. This may be due to the sewage sludge derived char with largely a heterogeneous carbon matrix contains less active adsorption site (surface area) for SO₂ and NO₂. Detailed surface characterization in terms of the active surface sites and surface functional groups is needed to make a thorough comparison.

In a separate study, H₂S was used to test the adsorption capacity of the sewage sludge derived char. It is found that sewage sludge char has fairly high adsorption capacity for H₂S. Compared with a commercial Calgon IVP carbon for odor control, the derived adsorbent has about 1/4 of the adsorption capacity of IVP carbon [6].

In the presence of water vapor and oxygen, coal reject derived sorbents are found to have much higher sorption capacity for SO₂ [11]. The sorption of SO₂ in the presence of water and oxygen results in H₂SO₄ formation in the sorbent particles. Metal oxides present in the coal reject char demonstrate catalytic effects on the sorption reaction. Thus the CRC has higher initial sorption rate than Ajax activated carbon. Figure 12 shows the dynamic uptake of SO₂ in CRC and Ajax particles at 150°C.

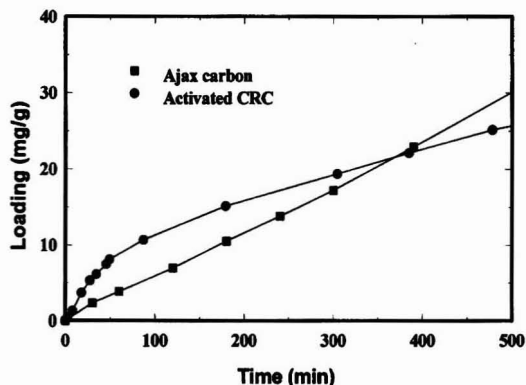


FIGURE 12 Dynamic uptake of SO₂ (SO₂: 1.0%, H₂O: 5.0%, O₂: 5.0%, 150°C).

CONCLUSIONS

In this paper, a new integrated process for SO₂ and NO_x removal using waste carbonaceous adsorbents is presented. The significance of using waste carbonaceous materials is two-fold: on one hand the waste materials are utilized or minimized; on the other, it can replace or partially substitute the expensive activated carbons for the removal of SO_x and NO_x.

A series of studies on the use of coal reject, sewage sludge and sawdust for the preparation of adsorbents have been conducted. Some fundamental aspects of preparing microporous adsorbents from these solid wastes are reviewed. Carbonization by pyrolysis in nitrogen atmosphere, physical activation in CO₂ and chemical activation by ZnCl₂ have been used to prepare adsorbents from these waste materials. Effects of process parameters on surface area development and pore structural evolution have been studied in detail. Adsorption characteristics of the wastes-derived adsorbents with respect to SO₂, H₂S, and NO_x have also been investigated.

It is shown that pyrolysis temperature, activation chemicals used and carbon burn-off are found to significantly affect the surface area development and pore structure evolution. An optimal pyrolysis temperature and hold time for maximum surface area development exists for all precursor materials. Physical activation of coal reject char after pyrolysis can improve the surface area of the derived chars, while chemical treatment in ZnCl₂ can enhance the microporosity of sewage sludge char. In physical activation, carbon burn-off or hold time is a critical factor in determining the surface char. Solution molar concentration of the activating agent is an important factor in chemical treatment of sewage sludge. It is observed that adsorbents prepared from solid wastes such as sawdust and coal mining wastes can be effective, promising adsorbents for SO₂ and NO_x removal from flue gases. Adsorbent derived from sewage sludge is a good adsorbent for odor control.

LITERATURE CITED

1. **Bansal, R. C., J. B. Donnet, and F. Stoeckli**, *Active Carbon*, Marcel Dekker, New York (1988).
2. **Chiang, P. C., and J. H. You**, "Use of Sewage Sludge for Manufacturing Adsorbents," *Canadian J. Chem. Eng.*, **65**, 922-927 (1987).
3. **Gray, P. G., and D. D. Do**, "Adsorption and Desorption of Gaseous Sorbates on a Bidispersed Particle with Freundlich Isotherm: II. Experimental Study of SO₂ Sorption on Activated Carbon Particles," *Gas Sep. Purif.*, **3**, 205-208 (1989).
4. **Gutierrez, M. D., et al.**, "Study of Subbituminous Coal Chars: Effects of Heat Treatment Temperature on Their Structural Characteristics," *J. Chem. Tech. Biotech.*, **41**, 85 (1988).
5. **Lopez-Gonzalez, J. D., et al.**, "Carbonization of Olive Wood: Evolution of Surface Area and Porosity with Treatment Temperature," *Adsorption Sci. Tech.*, **3**, 41-48 (1986).
6. **Lau, D. D.**, "Development of Adsorbent from Waste Materials for Air Pollution Control," MEng Thesis, Nanyang Technological University, Singapore (1994).
7. **Lu, G. Q., D. D. Do, and J. N. Beltramini**, "A New Process for SO₂ and NO_x Removal from Flue Gases," in *Chemeca 88*, Vol. 2, 1010-1017, C. J. D. Fell, ed., The Institute of Engineers Australia, Sydney (1988).
8. **Lu, G. Q.**, "Preparation and Characterisation of an Effective Sorbent for SO₂ and NO_x Removal Using Coal Washery Reject," PhD Thesis, University of Queensland, Australia (1991).
9. **Lu, G. Q., and D. D. Do**, "Preparation of Economical Sorbent for SO₂ and NO_x Removal using Coal Washery Reject," *Carbon*, **29**, 207-213 (1991a).
10. **Lu, G. Q., and D. D. Do**, "Structural Changes of Coal Reject Char During Pyrolysis at Low Heating Rates," *Fuel Processing Technology*, **28**, 247-258 (1991b).
11. **Lu, G. Q., and D. D. Do**, "Retention of Sulfur Dioxide as Sulfuric Acid by Activated Coal Reject Char," *Separations Technology*, **3**, 1-5 (1993).
12. **Lu, G. Q., J. C. F. Low, C. Y. Liu, and A. C. Lua**, "Surface Area Development of Sewage Sludge During Pyrolysis," *Fuel*, **74**, 344-348 (1995).
13. **Richter, E., K. Knoblauch, and H. Juntgen**, Mechanisms and Kinetics of SO₂ Adsorption and NO_x Reduction on Active Coke," *Gas Sep. Purif.*, **1**, 35-43 (1987).
14. **Singla, P. K., S. Miru, R. Hudgins, and P. L. Silveston**, "Pore Development During Carbonization of Coals," *Fuel*, **62**, 645-648 (1983).
15. **van Krevelen, D. W.**, *Coal*, Elsevier, Amsterdam (1961).
16. **Walker, P. L., Jr.**, "Coal Derived Carbons," *Carbon*, **24**, 379-386 (1986).

An Accurate Predictive Emissions Monitoring System (PEMS) For an Ethylene Furnace

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The Predictive Emissions Monitoring System (PEMS) has been recently proposed as an alternative to hardware continuous emissions monitors (CEM). PEMS has two distinct advantages over hardware CEM: much lower costs to install and maintain, and ability to provide information on emissions under various conditions. Using a state-of-the-art computer program, an accurate PEMS was developed for an ethylene furnace at Exxon Chemical Company's Baytown Olefins Plant, Baytown, Texas. First, a test plan was carefully designed to collect furnace process and stack emissions data over the total operating range of the furnace. The emissions data (NO_x , O_2 and CO) were collected and measured by an independent company for 5 days. The related process data were recorded in the DCS system during the same 5-day period. A dataset with some 7,000 patterns of related process and emissions data was generated. The PEMS system contains 2 parts: emissions prediction and sensor validation models. The main purpose of the sensor validation model is to validate the input sensor's raw data and reconstruct new sensor values, if necessary, before they are used in the prediction model. Its usage provides a high degree of confidence for the PEMS system. Two separate emissions prediction models were built, one for NO_x and O_2 , and the other for CO . Both final models have the same 9 input sensors. A PEMS relative accuracy test audit (RATA) was performed by an independent company to test the PEMS system under the three firing rate conditions (low, medium, and high). Test results indicate that the PEMS system satisfied both the relative accuracy (RA) and the stringent statistical test requirements including the F-test, t-test and r-correlation.

INTRODUCTION

Plants with sources of air pollutants may be required to continuously monitor their emissions such as carbon monoxide (CO), nitrogen oxides (NO_x), oxygen (O_2), sul-

fur oxides (SO_x), total reduced sulfur (TRS), and volatile organic compounds (VOC). The conventional method to monitor air pollutants is by using hardware continuous emissions monitors (CEM). An alternative solution is to use an alternative monitoring system (AMS) with the same or better precision, reliability, accessibility, and timeliness as that provided by CEM.

At the present time, the use of a computer program to predict air emissions is the only known and proven technology to qualify as an AMS. This computer technology for emissions prediction is known to industry as Predictive Emissions Monitoring System (PEMS), Alternative Continuous Emissions Monitoring System (ACEMS) or software CEM in contrast to its counterpart hardware CEM. Generally, PEMS utilizes a computer model to predict air pollutants using plant process, furnace, and stack gas emissions data as inputs.

This paper presents the development of an accurate PEMS system for the AF01 ethylene furnace at Exxon Chemical Company's Baytown Olefins Plant (BOP), Baytown, Texas.

SYNERGISTIC TEAM WORK

The successful completion of the Exxon PEMS project was made possible by the synergistic efforts and cooperation of several independent team members: Exxon Chemical Company—Baytown Olefins Plant, Baytown, Texas, Radian Corporation, Austin, Texas, Callidus Technologies Inc., Tulsa, Oklahoma, RAMCON Environmental Corporation, Memphis, Tennessee, and Pavilion Technologies, Inc., Austin, Texas. The main duties of each team member were as follows. Exxon BOP was the principal project coordinator and provided all process and furnace data for the AF01 ethylene furnace PEMS model training and testing, and participated in the emission data collection, PEMS model training and installation, and PEMS RATA test tasks. Exxon worked with Callidus to develop the initial data collection plan and the PEMS RATA test design. Radian was the principal contractor and project manager. Callidus performed the PEMS model training. Callidus also provided on-site

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support for the data collection and the RATA test. RAMCON performed the 5-day emissions data collection and the PEMS RATA test, and prepared the test report. Pavilion prepared the run time and interface codes for the PEMS system and installed the codes and the PEMS model on the Exxon BOP computer system.

PEMS FOR CONTINUOUS EMISSIONS MONITORING

The formation of emissions such as NO_x and CO in various furnace operations has been known to be affected by several dominant furnace variables. For instance, NO_x formation depends on furnace flame temperature and the amount of excess oxygen present. CO formation strongly depends on excess O_2 . A detailed discussion of NO_x formation and reduction can be found in Reference [1]. After a set of furnace variables is identified that affects the formation of NO_x and CO, we can develop models using these variables to predict them. These models must predict emissions data to satisfy both the Federal and State PEMS accuracy requirements. The term predict does not indicate that PEMS can forecast the furnace emissions in the future without any given furnace conditions, but rather that it can utilize historical data to predict furnace emissions on a real time basis.

There are two main approaches to developing models to predict emissions: first principles and empirical. Because of the complexity of furnace operations, first principles PEMS models are difficult to develop. If they exist, they are likely to be difficult to solve. Therefore, practical first principles PEMS models will very likely just be based on a few variables. Except in very ideal and simple furnace operations, these models are expected to produce inaccurate emissions calculations, but probably can project the trend of emissions formation.

Empirical PEMS models are developed using historical furnace and emissions data. They are usually much more accurate than first principles models, but do require historical data to develop models. For a modern chemical plant, this data requirement presents no problem as the plant will have readily available historical process data on its distributed control system (DCS). The only addition is collection of the emissions data for a given time period. Empirical modeling techniques range from simple linear regression using one or two variables to complex nonlinear regression using multiple variables. A final product of empirical PEMS will be a computer PEMS system to predict emissions continuously on a real time basis using related furnace data from the plant DCS.

PEMS SYSTEM—EMERGING TECHNOLOGY

Background Information

A cost effective, state-of-the-art computer PEMS system known as *Software CEM*TM has been developed by Pavilion Technologies, Inc., in Austin, Texas [2,3]. This PEMS system was licensed in late 1993 to Callidus Technologies Inc., a combustion and environmental company in Tulsa, Oklahoma, to develop PEMS systems for industry [4]. The first Pavilion PEMS was successfully developed, installed, tested and certified for a 221 MMBtu/hr boiler to monitor NO_x continuously at Arkansas Eastman in May, 1993 [5]. The Arkansas Eastman PEMS system has been running un-

der a state-issued operating permit since June 1993. This PEMS system is the first PEMS of its kind developed for commercial use in the U.S.

The PEMS system can be applied to boilers, gas fired turbines, crude oil heaters, ethylene furnaces, reciprocating engines and other furnaces that have electronically stored furnace data available. It may be used to predict NO_x , O_2 , SO_x , CO, TRS, VOC, and other emissions. Since its inception at Arkansas Eastman, more than 25 PEMS systems have been developed for various pieces of combustion-based equipment in the U.S.

How a PEMS System Works

The PEMS system contains two models: emission prediction and sensor validation [2,3]. Figure 1 illustrates the structure of a Pavilion *Software CEM*TM system with these two models [2]. Installation of a PEMS system can be on a modern workstation or a computer system that has access to the data historian. Depending on the state regulations for PEMS, the PEMS can be set to run at any time interval, e.g., 1-minute, 5-minute, etc., but usually not greater than a 15-minute time interval. The emission prediction model predicts emission variables such as NO_x and CO, given a set of furnace input variables or sensors such as firebox temperature, excess O_2 , and feed rate. Accurate prediction model output results depend on accurate input sensor values. During continuous running of the prediction model, any failed sensor readings could lead to erroneous emission prediction results.

In order to achieve the EPA-mandated 95% up-time requirement for an accurate PEMS system for continuous compliance, a sensor validation model was developed [2,3] as a precursor to the emission prediction model. During the PEMS system operation, the sensor validation model checks all the emission prediction model input sensor values from the DCS, activates alarms for failed sensors, and reconstructs their values from historical data before they are fed to the emissions prediction model. This dual model execution ensures a continuous and accurate PEMS system for emissions monitoring in compliance with governmental regulations. The emission prediction model results are fed to the plant DCS for display on one of its

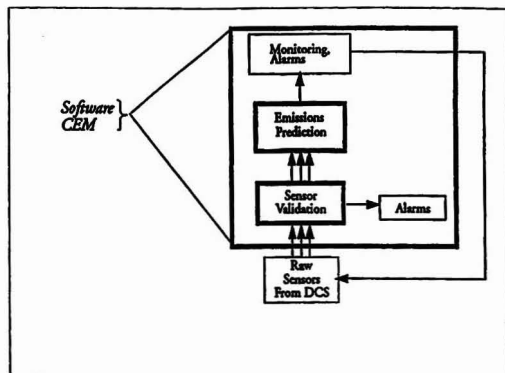


FIGURE 1 Schematic view of the structure of the *Software CEM*TM system including the sensor validation and prediction models (After Keeler et al. [2]).

consoles. The predicted emissions data are recorded in the plant database system.

An extensive mathematical analysis can be conducted to systematically fail sensors and determine the impact of each sensor failure on emission prediction model performance. This analysis can determine the maximum number of allowable sensor failures at which the model still predicts output results with a relative accuracy not to exceed a predetermined limit, e.g., 20%.

Adaptive Modeling

The furnace PEMS emissions prediction and sensor validation models are developed by Callidus using Pavilion's state-of-the-art *Process Insights*TM computer program. *Process Insights*TM is an adaptive modeling computer program. It uses proven nonlinear regression methods, fuzzy logic, chaotic systems, and advanced neural network learning algorithms. *Process Insights*TM is generic and can be used to model any system process that has sufficient input data. Models created by *Process Insights*TM are typically very accurate. *Process Insights*TM builds accurate PEMS models by learning the historical patterns of furnace process and related emissions data. In order to train an emission prediction model, usually about 3 to 5 days of stack emissions data such as NO_x and O₂ and the corresponding furnace process data are required. The stack emissions data are measured and collected by an independent stack data sampling company using certified hardware CEMs and following EPA emission measurement procedures. The furnace data are obtained from the plant DCS data historian. Figure 2 illustrates the process of gathering data to build a PEMS system.

PEMS VS. HARDWARE CEM

Decision to Install a PEMS

Exxon decided to install a PEMS on its BOP AF01 ethylene furnace because of its two main advantages over a hardware CEM. First, a PEMS appeared to bear much lower initial and long-term costs. Second, it has the capability to provide information on how furnace operations affect

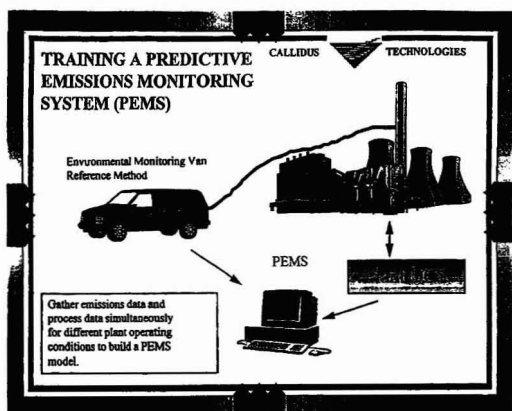


FIGURE 2 Schematic view of the process of data gathering to build a PEMS system.

emissions. However, in order to achieve complete success in a PEMS project, the quality of the furnace and stack emissions data must be good and consistent. Good understanding of furnace operations and emissions modeling skills are required.

General and Cost Comparisons of a Hardware CEM and PEMS

The application of a computer PEMS to accurately and continuously predict emissions in lieu of a hardware CEM can be a novel concept to some plant users and government regulators. Both systems monitor emissions, but are quite different in cost, methodology and maintenance. Table 1 compares the estimated costs at the time of preparation of the paper, and the advantages and disadvantages of a hardware CEM compared to a PEMS system [4, 6].

METHODOLOGY OF DEVELOPING A ROBUST PEMS SYSTEM

Based on Callidus' various PEMS project experience, the standardized steps in developing a reliable and robust PEMS system have been adopted to build the PEMS for the Exxon BOP AF01 ethylene furnace. The main steps are as follows. A detailed discussion on the methodology to develop a robust PEMS system can be found in Reference [4].

1. Design the data collection plan.
2. Contract a reputable, certified, independent stack sampling company to collect emissions data for approximately 5 days.
3. Record the furnace process data during the stack emission data collection.
4. Train the emission prediction model with all independent sensors that affect emissions.
5. Train the sensor validation model.
6. Thoroughly review PEMS models with in-house combustion and modeling experts and plant users. Remodel if necessary.
7. Prepare interface and run time codes for the PEMS models to install the PEMS system on the appropriate plant computer system. Test the installed PEMS real time.
8. Design the PEMS RATA (relative accuracy test audit) test plan for the installed PEMS system.
9. Contract a reputable, certified, independent stack data sampling company to perform a PEMS RATA test per Federal and State requirements to validate the installed PEMS system, and prepare a report of the RATA test results and the statistical calculations.

DEVELOPMENT OF A PEMS FOR THE EXXON BOP AF01 ETHYLENE FURNACE

General

The Exxon Chemical Company Baytown Olefins Plant (BOP) AF01 ethylene furnace was selected to be fitted with a PEMS to predict emissions. The installed PEMS performance will be evaluated against the PEMS regulations promulgated by the U.S. Federal government and the State of Texas. The PEMS protocol used in Texas was developed by the Texas Natural Resource Conservation Commission (TNRCC) in Austin, Texas.

For the BOP AF01 ethylene unit, the emissions to be monitored are NO_x, O₂, and CO. The unit has two kinds

TABLE 1 Comparison of Hardware CEM and PEMS Systems

Item	Hardware CEM	PEMS
Purpose	Monitors emissions continuously	Predicts emissions continuously
Estimated initial cost	\$150K ~ \$300K	\$75K ~ \$110K; Around 1/3 ~ 1/2 of a hardware CEM
Maintenance cost	High	Much lower than hardware CEM
Calibration gas cost	\$15K ~ \$30K per year	Not applicable
Cost for use as a backup to existing hardware CEM	High	Much lower than hardware CEM
Monitoring technique	Measurement	Prediction
Modeling	Not applicable; No modeling skills required	Requires modeling skills and expert knowledge in furnace operations
Data collection	Not applicable	Requires 3 ~ 5 days of furnace and stack emissions data
Accuracy	Medium to high	Can be as accurate (or more) as a hardware CEM
Recalibration	Requires personnel; 1 ~ 2 times per day	Recalibrated usually only on new stack tests; around 1 ~ 2 times per year, depending on state
Up time	Hardware can fail and a redundant system may be needed for backup to provide missing data during downtime	Practically 100% up as long as DCS is operational; Sensor validation model reconstructs failed sensor values; No redundant system may be needed
Secondary benefit	None	Provides insight into how furnace operations affect emissions; Can use PEMS models to optimize unit output and be in compliance in emissions levels

of furnace feed: naphtha and ethane. It undergoes decoke and regular operation cycles. Therefore, an accurate PEMS should be able to handle the naphtha and ethane feeds and the decoke and regular operations. Refinery gas is the main fuel for the furnace and it contains varying amounts of H₂. The AF01 unit also has an air preheater.

Development of AF01 PEMS Models

Using the above methodology to develop a robust PEMS, the PEMS models for the AF01 ethylene unit were developed by using the *Process Insights*TM computer program. The program was run on a Digital DEC 3000 alpha workstation at Callidus. First, a stack data collection plan was carefully designed to encompass all expected operating conditions of the AF01 furnace. In particular, the critical variables that will affect furnace performance and NO_x formation such as the furnace feed, firing rate, excess O₂, fuel composition, and air preheater status were to be perturbed during the data collection task. The data collection was performed during the period April 18 to April 23, 1994. A total of more than 5 days of stack emissions data of NO_x, O₂ and CO was collected on a 1-minute time interval. During the same period, the furnace process data were collected on a 1-minute time interval from the data historian of the DCS system. Prior to the data collection, all the process sensors were checked and calibrated if necessary to ensure reliable data recording. During the data collection task, a thorough cooperation between the plant personnel

and data sampling operators was required in order to achieve a successful data collection. This was accomplished in the AF01 PEMS project.

Altogether a total of 7,363 minutes or patterns of emissions and process data was collected. For the AF01 ethylene unit, two separate models were trained. The first was a combined NO_x and O₂ model that predicts both stack NO_x and O₂. The second was a CO model that predicts stack CO.

NO_x and O₂ Model

The measured O₂ for model training ranged from 2.98 to 14.06% with a mean of 6.83% and a standard deviation of 3.50%. The measured NO_x ranged from 26.49 to 160.73 ppm with a mean of 68.82 ppm and a standard deviation of 20.72 ppm. The first NO_x and O₂ model was trained using all 59 valid input variables. The stack NO_x (ppm) and O₂ (%) were the output variables. A sensitivity analysis was then performed to determine the significance or rank of each input variable in relation to the output variables. A high rank will indicate the variable has dominant influence on the output variables. Thus an input variable with rank #1 is the most influential on the outputs and an input variable with rank #59 in the first model practically would have very little or no influence on the outputs. By using the top rank inputs and expert knowledge of furnace and burner operations, the model training process using a smaller set of inputs was repeated. A final predictive NO_x and O₂

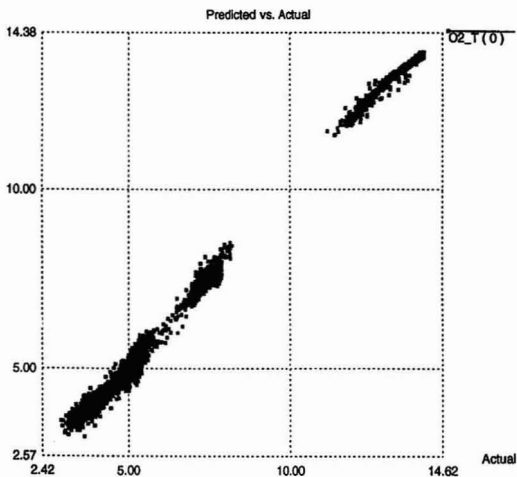


FIGURE 3 Predicted vs. actual O_2 scatter plot.

model was developed after several models were trained and rigorously tested and reviewed with Callidus and Exxon personnel.

The final NO_x and O_2 model has 9 input sensors. A sensitivity analysis of the effect of input sensors on NO_x and O_2 formation indicates that the primary sensors are excess O_2 , feed type, fuel gas density, and firing rate. The firing rate was determined to be the most important parameter affecting the NO_x formation. The final NO_x and O_2 model was trained using a total of 131 epochs with a train R^2 of 0.976 and a test R^2 of 0.980. The extremely high train and test R^2 indicate that the NO_x and O_2 data are highly correlative with the AF01 ethylene furnace process data. Also the Exxon AF01 process and the stack emissions data quality are very good, making this high correlation possible. Figures 3 and 4 show the predicted vs. actual (measured) plots (XY scatter plots) of all patterns (training and testing) for

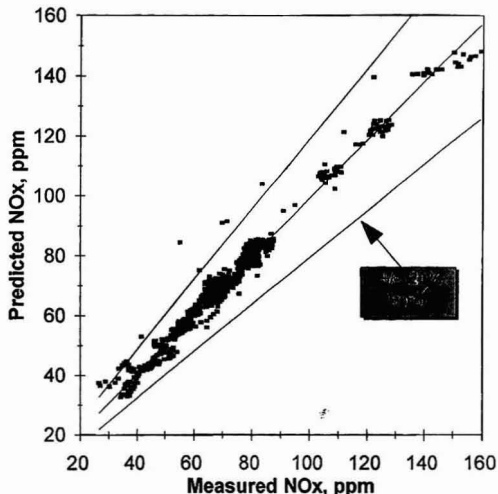


FIGURE 4 Predicted vs. actual NO_x scatter plot showing the lower and upper 20% error boundaries.

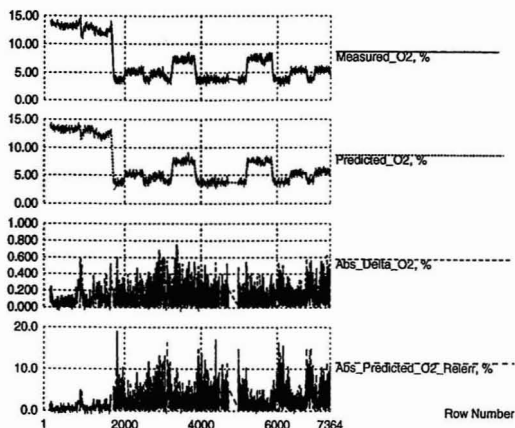


FIGURE 5 1-minute predicted vs. measured O_2 during model training; row number = pattern number.

O_2 and NO_x respectively. There is almost a perfect correlation between the predicted and the actual O_2 (Figure 3). The predicted and actual NO_x correlation (Figure 4) is very good but is not as good as the O_2 correlation. Also shown in Figure 4 are the usually allowable lower and upper 20% error boundaries enclosing the predicted vs. measured NO_x data. There are a few "abnormal" NO_x data points present in the dataset that may be real readings; they are shown in Figure 4 as the data points outside or close to the 20% boundaries. They were included for model training so that the model would learn to predict these anomalies.

Predictive O_2 Results

Figure 5 shows, on a 1-minute basis, the measured O_2 , model predicted O_2 , absolute difference between predicted and measured O_2 (Abs_Delta_ O_2), and the absolute value of the model predicted O_2 relative error (defined as (predicted O_2 -measured O_2)/measured O_2 * 100%).

Table 2 summarizes the model prediction results compared with measured values during model training on a 1-minute basis. As shown by Figures 3 and 5 and Table 2, the model predicted O_2 results are very close to the measured data, indicating the trained model can accurately predict stack O_2 emissions.

Predictive NO_x Results

Figure 6 shows, on a 1-minute basis, the measured NO_x , model predicted NO_x , absolute difference between predicted and measured NO_x (Abs_Delta_ NO_x), and the absolute value of the model predicted NO_x relative error (defined as (predicted NO_x -measured NO_x)/measured NO_x *100%).

Table 2 summarizes the model NO_x prediction results compared with the measured values during model training on a 1-minute basis. As shown by Figures 4 and 6 and Table 2, the model predicted NO_x results are very close to the measured data, indicating the trained model can accurately predict stack NO_x emissions. Figure 7 shows the plot of output NO_x , vs. % range of firing rate, indicating an almost linear relationship between NO_x and firing rate.

TABLE 2 Exxon BOP AF01 Ethylene Furnace: 1-Minute Measured and Predicted O₂, NO_x, and CO Data During Model Training

Name	Minimum	Maximum	Mean	Standard Deviation
Measured O ₂ , %	2.979	14.063	6.825	3.499
Predicted O ₂ , %	3.103	13.847	6.869	3.492
Abs. Delta O ₂ , %	0.000	0.757	0.135	0.108
Abs. Predicted O ₂ Rel. Error, %	0.000	18.997	2.618	0.108
Measured NO _x , ppm	26.492	160.732	68.817	20.722
Predicted NO _x , ppm	32.497	148.364	68.524	20.437
Abs. Delta NO _x , ppm	0.000	43.210	2.100	2.261
Abs. Predicted NO _x Rel. Error, %	0.001	54.602	3.293	3.925
Measured CO, ppm	0.000	57.904	1.179	3.443
Predicted CO, ppm	0.000	55.144	1.028	2.934
Abs. Delta CO, ppm	0.000	44.254	0.430	1.799

CO Model

The measured CO for model training ranged from 0.00 to 57.90 ppm with a mean of 1.18 ppm and a standard deviation of 3.44 ppm. A final predictive CO model was developed after several models were trained and rigorously tested and reviewed with Callidus and Exxon personnel.

The final CO model has the same 9 input sensors as those in the NO_x and O₂ model. The final CO was trained using a total of 9,901 epochs with a train R² of 0.851 and a test R² of 0.859. A lot of CO outliers were cut in the 5-day dataset and were not used in the CO model training, and 3,558 patterns remained valid for model training. The high R² indicated that the CO data were highly correlative with the AF01 ethylene furnace process data. Figure 8 shows the predicted vs. actual plot (XY scatter plot) of all patterns (training and testing) for CO. There were a few abnormal actual or measured CO points present in the data that were not cut from the model training because these data may represent true operations. They were included in the model training so that the model can learn to predict them.

A sensitivity analysis of the effect of input sensors on CO formation indicates that the two primary input variables are

the excess O₂ and firing rate. Generally, the stack CO formation would decrease as excess O₂ increases. The excess O₂ dominantly controls the CO formation as shown by its extremely high average sensitivity index. The CO formation has a nonlinear relationship with the firing rate. Figure 9 shows, on a 1-minute basis, the measured CO, model predicted CO, and the absolute difference between predicted and measured CO (Abs_Delta_CO). Table 2 summarizes the model CO prediction results compared with the measured values during model training on a 1-minute basis. For a predictive CO model performance, if the measured CO data are less than 25 ppm, the usual relative accuracy limit is not to exceed 5 ppm. As shown by Figures 8 and 9 and Table 2, the model predicted CO results are quite close to the measured data, indicating the trained model can accurately predict stack CO emissions. For instance, the 1-minute mean measured CO is 1.18 ppm with a standard deviation of 3.44 while the 1-minute mean predicted CO is 1.03 ppm with a standard deviation of 2.93. The absolute average difference between the predicted CO and measured CO is 0.43 ppm. The high train R² and test R² and

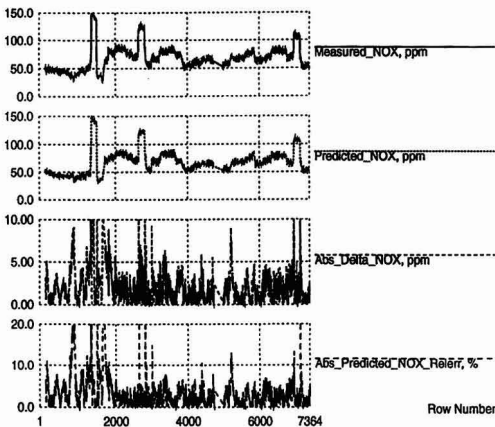


FIGURE 6 1-minute predicted vs. measured NO_x during model training; row number = pattern number.

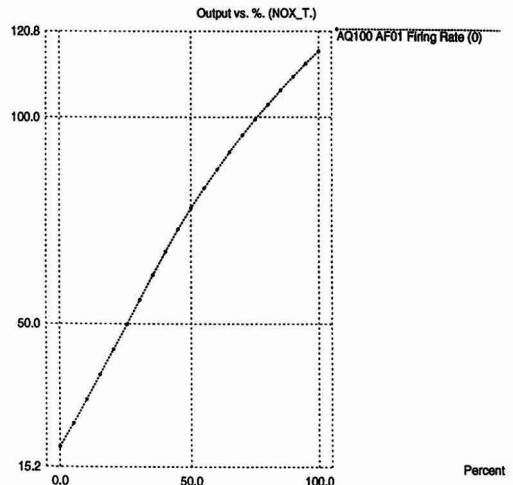


FIGURE 7 NO_x vs. % range firing rate.

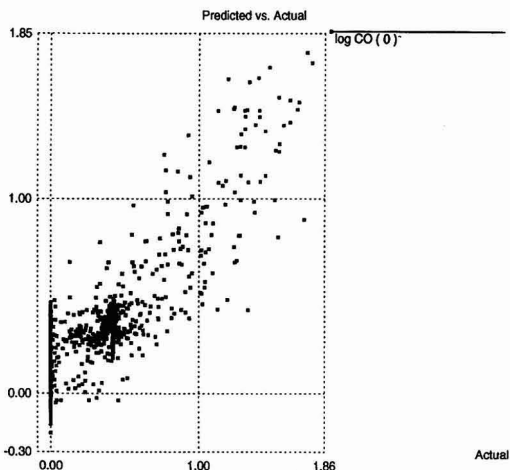


FIGURE 8 Predicted vs. actual log CO scatter plot.

the low difference indicate that the model will predict accurate CO results during real time execution. Figure 10 shows a highly nonlinear relationship between the CO formation and firing rate. CO increases rapidly when firing rate increases from 0 to 35% of its range and then decreases beyond the 35% range. This plot indicates that firing harder will require less excess O₂ (better mixing). However, beyond a certain firing range, the higher furnace temperature will burn the CO and subsequently the stack CO decreases.

Sensor Validation Model

After the predictive NO_x and O₂ model and the CO model were built, the sensor validation models for both predictive models were developed by using *Process Insights*TM. The same 9 input sensors in the NO_x and O₂ predictive model and CO model were used to build the sensor validation model for each predictive model. A train R² and a test R² greater than 0.96 were obtained for both sensor validation models.

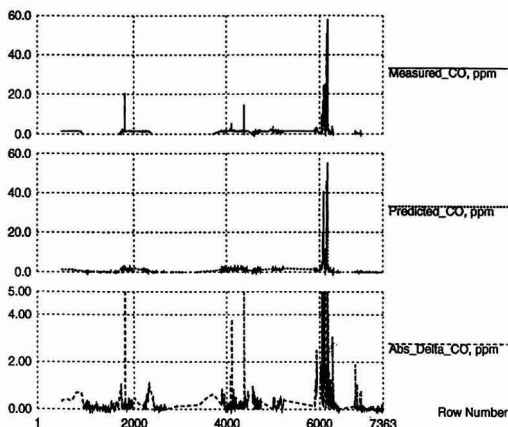


FIGURE 9 1-minute predicted vs. measured CO during model training; row number = pattern number.

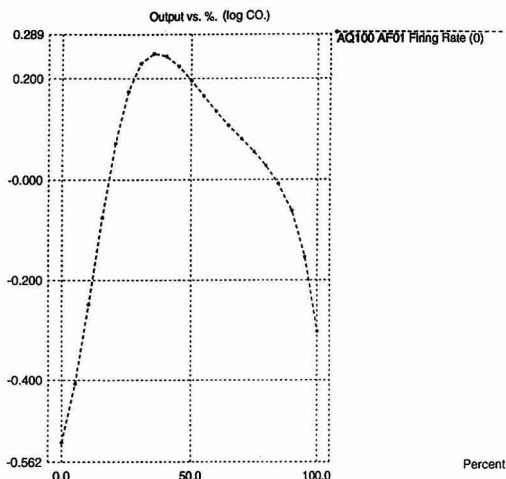


FIGURE 10 Log CO vs. % range firing rate.

PEMS Installation

After satisfactory predictive NO_x and O₂ and predictive CO models and their companion sensor validation models were built, a run time code was developed to execute the PEMS system. It was then installed and run on the Exxon BOP VAX 4000 Model 90 computer system using the Exxon proprietary interface system for input and output (I/O) operations. A console display was built to show the predicted CO, NO_x and O₂ and the status of the input sensor's alarms on a real time basis.

PEMS RELATIVE ACCURACY TEST AUDIT (RATA)—VERIFICATIONS, DESIGN AND RESULTS

Verifications

A PEMS Relative Accuracy Test Audit (RATA) was used to verify the performance and reliability of the installed PEMS system for the AF01 ethylene furnace. The test was performed by the same independent data sampling company that collected the 5-day data for model training. There are two main issues for a PEMS protocol: the emissions to be predicted, and the PEMS system performance specifications. In general, NO_x, O₂ and CO are the most common emissions to be modeled.

The Texas Natural Resource Conservation Commission (TNRCC) protocol addresses performing relative accuracy tests for its specified emissions of NO_x, O₂ and CO for the Exxon AF01 ethylene furnace. For instance, the usually acceptable relative accuracy for NO_x is not to exceed a 20% limit or be less than 5 ppm difference if the measured NO_x is less than 25 ppm. The relative accuracy for O₂ is not to exceed a 20% limit or be less than 1% difference. The relative accuracy for CO is not to exceed 5 ppm if the measured CO data are less than 25 ppm. In a relative accuracy test mandated by the TNRCC, a minimum of nine 21-minute data points for a pollutant such as NO_x at each of three specified levels of the input variable that affects the pollutant formation (NO_x) the most is required. Usually, three levels, low, medium, and high, of the input variable are set and the stack NO_x, O₂ and CO emissions are measured and

TABLE 3 Exxon BOP AF01 Ethylene Furnace PEMS RATA and Statistical Test Results, Baytown, Texas, May 19-20, 1994

Firing Rate	Low			Medium			High			Regulatory Limits
	O ₂	NO _x	CO	O ₂	NO _x	CO	O ₂	NO _x	CO	
RA	9.69%	2.75%	0ppm	5.81%	7.60%	1.18ppm	3.13%	2.53%	0.18ppm	≤ 20% or 5ppm
F-test	0.0018	0.0347	N/A	0.0075	0.2466	N/A	0.0011	0.0131	N/A	≤ 1.98
r-value	0.9648	0.8354	N/A							≥ 0.8
t-test	1.05	N/A	N/A							Bias adjustment

Based on the PEMS for this Exxon AF01 ethylene unit, firing rate is selected as the most important parameter that controls NO_x formation.

RA is relative accuracy.

r-value and t-test are calculated over the entire range of data collected for statistical test.

compared with the PEMS prediction results. TNRCC also requires performing additional stringent statistical tests including the F-test, t-test and r-correlation. The definitions and equations of relative accuracy, F-test, t-test and r-correlation can be found in 40CFR75. The purposes of the statistical tests are to verify the robustness of the PEMS system and to ensure that it can predict accurate results under the various operating conditions of the furnace.

Design

The design of a PEMS RATA test is different from the 5-day data collection test plan in that the data collection plan emphasizes collecting furnace and emissions data under all possible conditions of the important furnace operating parameters (or input sensors), while the RATA test focuses on having the models accurately predict NO_x, O₂ and CO at three levels of the critical furnace parameter that dominantly affects these emissions. The dominant parameters can be selected by the sensitivity analysis of the predictive emissions model. For the Exxon AF01 ethylene furnace, the firing rate was determined to be the most significant input variable affecting stack O₂, NO_x and CO formation. Also the authorized operating limits of the furnace were used to design the PEMS RATA test. A PEMS RATA test was designed to have two different feeds. The firing rate was to be operated at three levels.

PEMS RATA Test Results

A PEMS RATA was conducted on the installed Exxon AF01 ethylene furnace PEMS on May 19-20, 1994 [7]. The purpose of the PEMS RATA test was to provide results for demonstrating the PEMS compliance with applicable regulations. Those regulations set forth the PEMS tolerances. The State of Texas regulations stipulate that statistical tests be performed. The F-test, t-test, and correlation analysis were performed at each load level [7]. The stack emissions data of CO, NO_x and O₂ were subsequently compared to the Reference Method data values for determination of the relative accuracy (RA) of the PEMS and statistical values.

Table 3 shows the PEMS RATA and statistical test results for the PEMS installed on the Exxon AF01 ethylene furnace [7]. These results were calculated by RAMCON, the independent sampling company which conducted the PEMS RATA test for the AF01 unit. The results indicate that the

AF01 PEMS satisfied [7] the State of Texas PEMS RATA test for relative accuracy and the statistical tests. As shown in Table 3, the relative accuracy for NO_x in the three levels of low, medium and high firing rates are 2.75, 7.60, and 2.53%, respectively, which are far below the maximum allowable limit of 20%. The relative accuracies for O₂ at these 3 levels are 9.69, 5.81, and 3.13%, respectively, which are also significantly below the 20% limit. In general, the average expected relative accuracy for a hardware CEM is about 10% or less. Therefore, the AF01 ethylene furnace PEMS performs very well when compared with a hardware CEM based on the RATA test results. The F-test results for NO_x and O₂ are far below the maximum limit of 1.98. The r-values for NO_x and O₂ are 0.8354 and 0.9648, respectively, which are greater than the minimum allowable limit of 0.8. The t-test indicates that there are no bias adjustments necessary for NO_x and CO. A slight bias adjustment is recommended for O₂ (Table 3).

CONCLUSIONS

Based on the experience of developing the PEMS for the Exxon BOP AF01 ethylene furnace and the PEMS RATA test results, the following conclusions can be drawn. The PEMS developed and installed on the Exxon BOP AF01 ethylene furnace satisfied the PEMS RATA and statistical tests pursuant to the State of Texas PEMS protocol. The Exxon AF01 ethylene furnace PEMS is a very accurate predictive monitoring system that predicts O₂, NO_x, and CO with a relative accuracy much less than the maximum limit of 20% or 5 ppm. The PEMS probably is as accurate or more accurate than a comparable hardware CEM system. The PEMS can be very cost effective. The firing rate dominantly controls the NO_x formation in the AF01 ethylene furnace. The excess O₂ dominantly controls the CO formation in the AF01 ethylene furnace. Adaptive modeling is very powerful and can discover correct interrelationships between output variables and input variables. The success of a PEMS project depends on a complete data test plan that includes all normal furnace operating regimes. Good quality measurements of stack emissions data and furnace data are also required to achieve a successful PEMS project. The PEMS system has been shown to work very well in the AF01 ethylene furnace and is expected to do well in other kinds of furnaces that have quality data.

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LITERATURE CITED

1. **Martin, R. R.**, "NO_x Control, Formation, Minimization, Reduction," Technical Paper, Callidus Technologies Inc., Tulsa (Apr. 1990).
2. **Keeler, J., J. Havener, E. Hartman and T. Magnuson**, "Achieving Compliance and Profits with a Predictive Emissions Monitoring System: Pavilion's *Software CEM*TM," Pavilion Technologies Technical Report, Austin (1993).
3. **Havener, J., and K. Terhune**, "Implementation of a *Software CEM*TM for NO_x Emissions Monitoring," paper presented at the 1993 Fall International Symposium, American Flame Research, Tulsa (Oct. 1993).
4. **Cheng, A. M., R. R. Martin and A. K. Reyburn**, "Callidus' First Year Experience with Predictive Emissions Monitoring Systems (PEMS)," paper presented at the Chemical Engineering Chemputers III Conference & Exhibition, Houston (Feb. 1995).
5. **Collins, M. and K. Terhune**, "A Model Solution for Tracking Pollution," *Chemical Engineering*, pp. 32-37 (June 1994).
6. **Samdani, S. G.**, "Software Takes on Air Monitoring," *Chemical Engineering*, pp. 30-33 (Dec. 1994).
7. "NO_x, CO, and O₂ PEMS Relative Accuracy Test Audit, May 19-20, 1994, Source AF-01," report prepared by RAMCON Environmental Corporation, Memphis (June 1994).

An Industrial Wastewater Pollution Prevention Study: Evaluation of Precipitation and Separation Processes

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A water pollution prevention study was performed for two plating processes at Lawrence Berkeley National Laboratory (LBNL). This study included wastewater precipitation process analysis, and evaluation of separation and recycling alternatives. One of the pollution prevention opportunity assessment goals is to reduce and reuse wastewater.

From a review of coordination chemistry and a series of precipitation process tests, it was found that treatment with optimized pH and mixing rate, proper coprecipitants (such as iron salts), and chemical dosages were needed to dissociate metal ions from the complexes in the wastewater. In this study, reverse osmosis and ion exchange technologies were also evaluated. A water reclamation analysis with these two technologies was implemented. The analysis projected, that with recycling systems, 33% of the wastewater could be reclaimed.

INTRODUCTION

In LBNL, there are two plating-related shops. These plating processes involve (a) acid cleaning, microetching, electroless copper deposition, ferric chloride etching, electroplating (copper and tin/lead), and soldering in one shop, and (b) acid copper, bright nickel, electroless nickel, and anodizing baths in the other shop.

Currently, these two processes generate 103,000 liters of wastewater each week. In 1996, the total quantity of wastewater generated by these two plating facilities will be increased fourfold. Since one of the pollution prevention goals of LBNL is to conserve water and reduce hazardous wastes [1], and since it has been found that more than 99% (volume) of the total waste stream generated by the plating processes was water [2], a water pollution prevention opportunity assessment was conducted. In this study, plating process (a) was selected as a protocol to identify waste minimization measures.

In process (a), the copper or other metals concentrations and total dissolved solids (TDS) in the wastewater samples taken from the floor sump and the holding tank of treatment process were in 100 mg/l and 3,000 mg/l range, respectively. The floor sump usually collects wastewater and solutions from process rinses and sink rinse. The collected wastewater is then pumped to an existing treatment system. This treatment system used in plating process (a) consists of acidification, neutralization, flocculation, and clari-

fication and filtration steps. It has 38 liters/min treatment capacity. After being treated by this treatment process, the treated water is then sampled prior to discharge to the sewer. The plating shop normally can reduce copper concentrations in its wastewater below 2.0 mg/l, which is the discharge limit.

However, complexing agents, such as amine, citric, and tartaric acids, or other organic chelators used in the electroless copper (or nickel) solution were occasionally causing metal precipitation problems. In order to reduce wastewater treatment cost, and select efficient treatment and water reclamation alternatives, two studies were performed: (1) precipitation process and coordination chemistry analysis and (2) evaluation of separation technologies.

PRECIPITATION PROCESS ANALYSIS

In order to compare the precipitation technique with other water separation/reuse alternatives, a summary of the coordination chemistry is presented below. A brief review of the precipitation and coagulation mechanisms was presented in our previous paper [2].

Coordination Chemistry

In aqueous solution, free metal ions are coordinated with molecules or anions containing free pairs of electrons to achieve stabilization. This reaction is called coordination or complex formation and can be covalent, electrostatic, or a mixture of both. Those molecules or anions (including water and hydroxyl ions) with which metal ions form coordinated complexes are referred to as bases or ligands. Typical examples of organic ligands which can occupy more than one coordination position in the complex are ethylenediamine, citrate, carboxylate, ethylenediamine tetraacetate (EDTA), nitrilotriacetate (NTA), phosphate, and other organic compounds which have electron donor groups [3-5].

When organic chelating ligands are not available or their concentrations are low in aqueous solutions, metal ions are normally hydrated with water molecules or hydroxyl ions to form aquo complexes. In general, the percentage of the hydrated species increases as the pH increases. However, when organic chelating ligands exist in aqueous solution, the combination of a metal ion with donor groups of chelating ligands will displace water molecules or hydroxyl ions of aquo complexes.

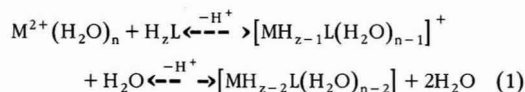
The complexing capacity of metal ions with organic chelating ligands also increases as the pH increases [5]. This might be caused by formation of mixed $M(H_zL)(OH)_n$ complexes where M represents metal ions, H_zL is the ligands, and n and z are integers. A complexing reaction can take place with chelating ligands where more than one atom in the ligand can associate with the metal ion and form complexes. For example, the chelating ligand EDTA can attach a metal ion at six coordinative sites because EDTA has two amino (CH_2-N) and four carboxylate ($-COO^-$) electron donor groups [4].

(1) Dissociation and Formation Reactions

In general, because various species in aqueous solution are in a formation-dissociation equilibrium, displacement reactions of one metal or ligand by another are possible. The extent of displacement and formation depends on the relative stabilities of the complexes in water. Their stabilities depend on the characteristics and concentrations of metal and ligands, the number and the orientation of the donor groups of ligands, the number and size of metal chelate rings formed, and the pH.

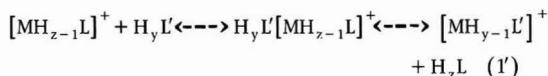
For most of metal-ligand complexes, formation of rings by the organic chelating ligands contributes extra stability from the entropy effect of displacing hydrated water molecules. Therefore, they are relatively more stable than hydrated metal ions or metal salts. The complexing capacities of different metal and hydrogen ions with ligands are different. Thus different metal-ligand complexes have different stabilities in aqueous solutions. For example, in a broad range of pH, the complexing capacities for cupric ($2+$) ions are higher than for other metal ions, such as Cd^{2+} , Ca^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} [5, 6]. This is also due to the fact that Cu^{2+} forms different structures of complexes with humic substances or other organic ligands than does Mn^{2+} , and other metal ions.

Since metal cations also compete with hydrogen ions for the available electron donor groups of ligands, the pH of aqueous solutions strongly influences the stabilities or the dissociation-formation reaction of metal-ligand complexes [7]. For example, at low pH values, the combination of hydrogen ions with electron donor groups of ligands will free metal ions from metal-ligand complexes. Thus free metal ions will be hydrated with water molecules or hydroxyl ions. Since water dissociates into hydrogen and hydroxyl ions, which are in the system of simultaneous equilibria, it is a competing ligand of metal ions. The following equation shows an example of the dissociation of hydrogen ions from a ligand (H_zL) or the formation reaction of metal-ligand complexes.



where n and z are integers. In this dissociation-formation reaction, when the pH is low, the reaction proceeds to the left, which means the hydrated metal ions are relatively more stable than the metal-ligand complexes. In reality, the dissociation-formation reaction of the complexed metals in wastewater or natural water is more complicated than Equation (1). It depends on the presence of other ligands,

metal ions, and the solution pH [6, 8]. The ligand-exchange reaction described below is influenced by steric and electrostatic factors and by the availability of electron donor groups of the incoming ligand (L').



where y is an integer. This reaction may influence the Equation (1).

(2) Hydrolysis and Precipitation Processes

As hydrolysis of metal ions occurs, the sizes and surface charge of the ionic species increase. When the colloid surface becomes charged, a charged double layer surrounding the colloid is formed. The existence of these double layers around colloids inhibits the close approach of colloids to each other [9]. Thus the colloids or hydrated metal ions may be stabilized to remain in suspension in solution.

In order to precipitate metal ions as salts out of wastewater, the hydrated metal ions must be destabilized. Factors influencing destabilization mechanisms include type and dosage of coagulant, pH, chemical composition of the wastewater, and mixing conditions [10]. For example, upon addition of coagulants to the wastewater and adjusting the solution pH, it results in the production of positively and negatively charged colloids. The electrostatic attraction between these charged groups enhances the reductions of surface charge and the thickness of double layer. Since metal hydroxides have been shown to precipitate most rapidly and with minimum solubility in a narrow pH range, the destabilization process can be carried out within the optimum pH zone for the solution. Because the colloids have been destabilized, they can stick to each other and result in particle growth.

From the review of coordination chemistry, we found that the removal of metal ions from wastewater involves two critical steps:

- the dissociation of metal ions from metal-ligand complexes with optimum pH adjustments, and
- the reduction of double layers of hydrated metal ions with pH adjustments and coagulants.

After these two steps, the incorporation of metal ions into suspended solids, and the subsequent growth and sedimentation of metal flakes can be achieved and enhanced by adding co-precipitants and polymer flocculants into wastewater and by proper mixing.

In this study, a series of treatment tests with different coagulants, chemical dosages, and pH ranges were conducted. A portion of the test results are summarized below. The detailed description of the results can be found elsewhere [2].

Laboratory Analysis

(1) Original Treatment

Wastewater samples taken from both the holding tank and rinse after the electroless copper bath (copper concentrations were 9 and 45 mg/l, respectively) were treated with

sulfuric acid (added to bring the pH < 3), ferric chloride (FeCl₃), sodium hydroxide and lime (to bring pH up to 9–9.5), and polymer flocculant. The concentrations of ferric chloride used for these two tests were 1,300 and 600 mg/l, respectively. Both treated samples showed blue color when the pH was above 3.5. (The blue solution was also observed in the process treatment of the wastewater.) After treatment, copper concentrations in both solutions were still above 5.0 mg/l. The flakes formed in both samples settled in one hour.

However, tests of rinsewater from micro-etch, accelerator, catalyst, surface cleaning, sulfuric acid, and electroplating copper and tin/lead rinses with similar treatment procedures as the above two tests did not show a blue color. The test results showed that copper concentrations in the treated solutions were in the range of 0.5 to 3.3 mg/l, and flakes settled in 30 minutes.

Several other tests of wastewaters containing the electroless copper rinsewater with different dosages of caustic soda, lime, ferric chloride, or other coagulants were also performed. However, at the pH of 9.0, the test results were not promising. After treatments, the copper concentrations in wastewaters were greater than 5 mg/l and the treated samples showed blue color. This indicated that wastewaters were contaminated by chelating ligands (the electroless copper rinsewater contains chelating ligands). Thus in order to treat the wastewater containing metal-ligand complexes, higher dosages of coagulants, different coagulants, and optimum pH control were tested.

(2) Treatment Alternatives

Wastewater samples from the floor sump where copper concentrations were in the range of 90 mg/l were also treated with sulfuric acid (added to bring the pH < 3), ferrous sulfate (FeSO₄·7H₂O), sodium hydroxide and lime (added to bring pH up to 6.6–8.8), and flocculant. The tests showed that with 530 to 1,300 mg/l of ferrous sulfate, the copper concentration could be reduced to less than 1.0 mg/l when the pH was above 6.0. No blue solutions were observed in these tests.

Tests with high dosages of ferric chloride were also performed with wastewater samples. The original copper concentration of wastewater taken from the holding tank of the treatment system was 16 mg/l. Wastewater samples were treated with about 5,000 to 6,800 mg/l of ferric chloride solution (containing 27 to 45% of ferric chloride) to bring the final copper concentration of the sample down to 1.0 mg/l or less when the pH was in the range of 9.0 to 9.5.

A series of pilot process tests was also performed with the existing treatment system. For example, a batch of wastewater containing 16.0 mg/l copper was treated through the precipitation system. After being processed five times in the treatment system, each time with sulfuric acid, 800 to 1,000 mg/l of ferric chloride, sodium hydroxide and lime (added to bring the pH up to 9 to 9.5), and flocculant, the copper readings of effluent samples were reduced to 4 mg/l. (During these process treatments, the wastewater in the treatment chambers was blue.) This indicated that in order to reduce the copper concentration to less than 1 mg/l, a high dosage of ferric chloride (≥ 5,000 mg/l) will be needed.

A series of treatments with ferrous sulfate was also performed to treat the sump wastewater. For example, several

batches of wastewater containing 30 to 94 mg/l copper were treated with sulfuric acid, 530 to 1,300 mg/l of ferrous sulfate, sodium hydroxide and lime (added to bring the pH up to 6.6–8.8), and flocculant. Treatments reduced the copper concentrations to less than 0.6 mg/l. Partial results are presented in Table 1.

In this study, it was found that in addition to a lime and caustic soda treatment, destabilization of the metal complexes with acids and co-precipitants was required. The destabilization was successfully achieved by first lowering the pH to less than 3.0 with acids. At low pH, [H⁺] can free metal ions from chelating agents by coordinating itself with the ligand (see Equation 1). After freeing the Cu²⁺ from the complex, a co-precipitant, such as ferrous sulfate or ferric chloride was added to the wastewater. Then the solution was mixed with lime and caustic soda to bring the pH up to 6.6–8.8 for the treatment with ferrous sulfate or to 9.0–9.5 for the treatment with ferric chloride and flocculants to enhance the growth and sedimentation of metal-flocculant flakes.

(3) Effects of Other Metal Ions

Other metal ions, such as nickel, lead, zinc, or chromium, were also identified in the plating wastewater of process (a). Their concentrations in wastewaters were in the range of 0.5 to 38 mg/l. It was found that after treatments, their concentrations could always be reduced to either non-detected level (ND) or less than 0.5 mg/l (see Table 1). The test results indicated that these metal ions have no or very little effect on the Cu-ligand complexing process and the removal of copper ions from the tested wastewater.

Table 1 shows that the removal of nickel is less efficient than that of lead with either ferrous sulfate or ferric chloride treatments. However, the removal of lead and zinc ions from wastewater samples were about the same. The test results also indicated that the complexing capacities for cupric (2+) ions are higher than for Ni²⁺, Pb²⁺, or Zn²⁺. It is consistent with the stability of metal-ligand complexes which follows the sequence of Zn²⁺ < Pb²⁺ < Ni²⁺ < Cu²⁺ [2–4].

(4) Summary

The results of the above tests indicated that

- (1) both ferric chloride and ferrous sulfate can be used as co-precipitants to treat wastewater containing metal-ligand complexes; however, the wastewater treatment with ferrous sulfate is more efficient than that with ferric chloride,
- (2) the interrelations between the required co-precipitants, the chemical dosage, and the optimum pH of the solution strongly influence the metal removal result,
- (3) the flakes generated by the ferrous sulfate treatment settled slower (in hours) than those generated by the ferric chloride treatment (in an hour),
- (4) although both ferrous sulfate and ferric chloride treatments could reduce metal concentrations below 1 mg/l, the contents of TDS in treated wastewaters were still high (in the range of 3,000 mg/l),
- (5) the presence of other metal ions, such as nickel, zinc, lead, or chromium, in the wastewater has little effect on the removal of copper ions in solutions, and

TABLE 1. Summary of the Precipitation Tests with Iron Salts

Treatment	Chemicals	Original Conc., mg/l	Final pH	Efflu. Conc., mg/l	Comments
FeCl ₃ #1	Copper	16.0-94.0	9.0	1.00	Sump wastewater treated with FeCl ₃ sol'n (6,750 mg/l) by bench test
	Nickel	unknown		unknown	
	Lead	unknown		unknown	
FeCl ₃ #2	Copper	16.0-94.0	9.3	2.50	Sump wastewater treated with FeCl ₃ sol'n (4,500 mg/l) by bench test
	Nickel	0.96		0.15	
	Lead	0.25		ND	
FeCl ₃ #3	Copper	9.10	10.0	6.50	Process wastewater treated with FeCl ₃ sol'n (810 mg/l); by process test
	Nickel	0.50		0.41	
	Lead	0.04		0.02	
FeCl ₃ #4	Copper	6.50	9.4	4.04	Process wastewater treated with FeCl ₃ sol'n (1,620 mg/l) by process test
	Nickel	0.41		0.22	
	Lead	0.02		0.01	
FeCl ₃ #5	Copper	45.0	9.0	5.01	Electroless rinsewater treated with FeCl ₃ sol'n (600 mg/l) by bench test
	Nickel	ND		ND	
	Lead	ND		ND	
FeSO ₄ #1	Copper	60.0	6.6	0.68	Sump wastewater treated with FeSO ₄ ·7H ₂ O (528 mg/l) by process test
	Nickel	unknown		0.38	
	Lead	unknown		ND	
FeSO ₄ #2	Copper	61.0	7.9	0.43	Wastewater treated with FeSO ₄ ·7H ₂ O (600 mg/l) by process test
	Nickel	4.70		0.51	
	Lead	6.90		ND	
FeSO ₄ #3	Copper	16.0	8.5	0.55	Sump wastewater treated with FeSO ₄ ·7H ₂ O (1,250 mg/l) by bench test
	Nickel	0.96		0.15	
	Lead	0.25		ND	
FeSO ₄ #4	Copper	30.0	8.1	0.24	Sump wastewater treated with FeSO ₄ ·7H ₂ O (1,000 mg/l) by process test
	Nickel	3.30		0.11	
	Lead	6.0		ND	
FeSO ₄ #5	Copper	94.0	8.8	0.27	Process wastewater treated with FeSO ₄ ·7H ₂ O (1,000 mg/l) by process test
	Nickel	3.80		0.17	
	Lead	4.90		ND	

(6) the ligand complexing capacities for Cu²⁺ are higher than for Ni²⁺, Pb²⁺, or Zn²⁺.

EVALUATION OF SEPARATION TECHNOLOGIES

Although the precipitation process with ferrous sulfate or ferric chloride can greatly reduce copper concentration in wastewater, this plating process (a), combined with plating process (b), will discharge 24 million liters/year of wastewater to the sewer. Since water conservation is important for these two plating processes and is also one of the pollution prevention goals of LBNL [1], two water reclamation and recycling processes were designed for these plating processes. Separation alternatives were evaluated, including reverse osmosis (RO), ion exchange (IX), electrolytic deposition or electrowinning (EW), and evaporation (EV). Similar closed-loop studies can be found elsewhere [2, 11-15].

A technical and economic analysis of these separation alternatives was conducted. The total annual cost includes the costs of operation and maintenance, labor, chemicals, permitting and regulatory compliance, and waste disposal.

The summary of this evaluation is presented in Table 2. A technical review of the RO and IX technologies is described below as is the recycling process analysis used for the plating process (a).

Membrane Filtration

(1) Membrane Separation Technology

Membrane separation technology consists of the following four major techniques: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) filtration. MF removes particles in the range of 10 to 100 microns in diameter, such as pigment and gelatin. UF membranes provide filtration in the 1.0 to 10 micron range. It can remove substances, such as colloidal silica, latex emulsion, or carbon black. NF removes particles in the 1.0 to 10⁻¹ micron range. It rejects selected salts and most organics.

RO rejects particles as small as 10⁻¹ to 10⁻³ microns in size, which include ionic materials, dissolved salts, and most organics. RO normally operates on the concept of

TABLE 2. Evaluation of Five Different Separation Technologies

EVALUATION	REVERSE OSMOSIS	ION EXCHANGE	ELECTROLYTIC CELL	EVAPORATION	PRECIPITATION
Waste quantity	low	low-medium	low-medium	low	substantial
Water recovery	high	high	low	medium	low
Effluent TDS	20 ~ 35 ppm	~ 1-10 ppb	~ 100 ppm	~ 50 ppm	1,000-3,000 ppm
Closed-loop potential	high	high	low	low-medium	low
Operat'n/maint.	~ \$3K/yr	~ \$3K/yr	\$3-5K/yr	~ \$3K/yr	\$5-8K/yr
Chemical usage	low	medium	low	zero-low	medium-high
Permit	no	no	no	yes	yes
Energy	low	low	medium	medium-high	medium
Space	medium	medium	medium-large	small-medium	large
Labor	medium	medium	medium-high	high	high
Overall	good	good	fair-good	fair-good	fair
Capital costs and capacity	\$30-40K 20 liter/min	\$25-40K 20 liter/min	\$25-45K 400-800 liter	\$20-40K 200-400 liter/hr	\$40-65K 20-50 liter/min

crossflow. Pressure in the system forces water through the membrane. The concentrated or rejected solution is usually recycled back to the process. A detailed review of membrane technology can be found elsewhere [13-16].

(2) RO Modules and Membranes

Commercially available membrane modules can be classified into four basic types: (1) tubular, (2) spiral wound, (3) hollow fiber, and (4) plate-and-frame. The first one requires considerable floor space and has relatively high capital costs [16]. The second and third modules have similar cost-to-capacity ratios. Hollow-fiber modules need less space, while spiral-wound units are less easily plugged by suspended solids. Since the membrane fouling propensity of the spiral-wound module is normally higher than those of the other three modules, it is the most widely used configuration in the RO industry. However, the ease of cleaning of the spiral-wound module is poor to medium.

The application of RO to the treatment of metal plating waste streams is often limited by the pH range in which the membrane can operate. Three types of semipermeable membrane materials can be used in RO units: (1) cellulose acetates (acetate, diacetate, and triacetate), (2) aromatic

polyamide, and (3) thin-film composite membranes. The cellulose acetate membranes have a narrow pH range, which varies from 2.5 to 8 [13]. The allowable pH range (4 to 11) for polyamide membranes is broader than that for cellulose acetate [13, 14]. The potential of high acidity in plating wastewater makes both cellulose acetates and polyamide membranes unsuitable for treating this kind of wastewater, unless pretreatment by adjusting the pH value is applied. The thin-film-composite membranes appear to result in a membrane that is least affected by pH (ranges from 1 to 12) [13, 17]. A brief comparison of these three types of membranes with two different modules is presented in Table 3.

Normally, the membrane performance, such as permeate flow and rejection coefficient, decreases with operating time [15]. The reasons for these decreases can be

- clogging of the membrane by precipitants,
- fouling of the membrane by oxidizing chemicals and/or solvents,
- deterioration of the membrane by high concentrations of acidic or alkaline solutions, and
- normal compaction, wear, or tear of the membrane by the applied pressure.

TABLE 3. Characteristics of Membranes Used for Reverse Osmosis

Characteristics	Spiral-wound cellulose acetate	Hollow-fiber polyamide	Hollow-fiber cellulose acetate	Spiral-wound thin-film composite
pH stability	2-8	4-11	4-7.5	1-12
Fouling resistance	good	poor	poor	good
Oxidation resistance	good	poor	fair-good	fair
Max. salt rejection, %	90-98	90-99	90-99	90-98
Allowable chlorine, ppm	0.2-2.0	< 0.05	0.3-1.0	0.05-1.0
Temperature, °C	35	35	30	29

In order to minimize any damage to the membrane during operation, the RO user should backwash the membrane, observe the pressure and pH limits, and examine the specific membrane flux data frequently. The specific membrane flux can be estimated with Equations (2), (5), and (6) described below. A particle filtration unit in front of the RO is usually needed to prevent clogging of the membrane. For the inhibition of biological growth, the RO elements should be immersed in a protective solution, such as a glycerin and sodium bisulfate solution. It is also recommended that after initial wetting, the elements should be kept moist at all times.

(3) RO System Design Parameters

The RO system design should consider several parameters: (1) water characteristics (dissolved and suspended solids, temperature, pH, viscosity, osmotic pressure, etc.), (2) pretreatment requirements (filtration or neutralization), (3) membrane features (materials, module arrangement, cleaning requirements, applied pressure, flow rates, minimum flux), and (4) integration with other processes. These factors will influence the flux and percent rejection, which define system size requirements and effluent quality, respectively.

In RO, particles and dissolved solids are separated from water by applying a hydrostatic pressure greater than the osmotic pressure of the feed stream. This pressure requirement limits the practical application of this technology. The osmotic pressure of a stream containing solutes can be rather high, even at relatively low solution concentrations.

The trans-membrane flux (permeate flow) is a function of hydrodynamic permeability and the net pressure difference between the feed and permeate solutions. On the basis of the solution-diffusion model, the water flux through the membrane is defined as

$$J_w = A(\Delta p - \Delta \pi) \quad (2)$$

where Δp is the hydrodynamic pressure difference between the feed and permeate across the membrane, $\Delta \pi$ is the osmotic pressure difference between the feed and permeate at the membrane surface, J_w is the flux (which is the volume flow of permeate per unit membrane area), and A is the pure water permeability constant or the specific membrane flux (which depends on water temperature, water diffusivity, resistance due to solute absorption on the membrane, and water concentration in the membrane). The flux is proportional to the effective pressure driving force and decreases with increasing feed concentration (i.e., higher feed concentration requires larger operating pressure). In practice, the applied pressure normally ranges from 1.4 to 6.8 MPa [13, 17].

The separation capability of a membrane can be expressed in terms of percent rejection, which is defined as the concentration difference between feed stream (C_f) and permeate (C_p) divided by the feed concentration. The following equation describes the definition:

$$r = 1 - C_p/C_f \quad (3)$$

where r is the percent rejection of a membrane for a given

component at a hydrostatic pressure and feed solution concentration. A higher percent rejection will result in better quality of permeate and concentrated stream. Percent rejection is primarily affected by the membrane type, although it will decrease with increasing feed concentration. A high percent rejection (normally between 90% and 99%) is reached for most cations [13, 16].

The recovery rate, defined here as the feed volume (V_f) that is converted to permeate volume (V_p), ranges from 90% to 99% [13, 17] in several examples. It is described in the following equation.

$$R = V_p/V_f \quad (4)$$

The recovery rate is a strictly operational parameter, which is not directly linked to the membrane. Because the concentration in the concentrated stream is limited by osmotic pressure and viscosity, the water (permeate) can never be completely recovered as pure permeate. The concentration in the permeate is not only determined by the membrane percent rejection, but is also a function of feed solution concentration and recovery rate.

A knowledge of osmotic pressure is necessary to properly design a RO system. From a practical approach, the difference in osmotic pressure can be estimated directly from the TDS in a particular feed water or the conductivity of the effluent [13, 15]. When the feed solution temperature is 25°C, the approximate equation is given as follows:

$$\Delta \pi \approx 0.0069 \text{Kr} [0.5(\text{TDS}_f + \text{TDS}_c)] \approx f \cdot C \quad (5)$$

where $\Delta \pi$ is in MPa; K is the osmotic constant (which is given as $355(\sum M_i)/\text{TDS}_f$); TDS_f and TDS_c are total dissolved solids in the feed and concentrated solutions, respectively; M_i is the molar concentration of individual ions; r is the solute percent rejection; C is the conductivity of the effluent; and f is a constant which can be calculated by fitting experimental data into Equation (6).

$$J_w/\Delta p = A - (C \cdot A \cdot f)/\Delta p \quad (6)$$

(4) Four Membrane Separation Modes

Depending on the concentrations and hydrostatic pressures in the feed and permeate, four different membrane separation modes exist [17].

- (1) *Chemical Equilibrium.* The concentration and the hydrostatic pressure in both feed and permeate are equal; thus no net flux of solute occurs across the membrane.
- (2) *Osmosis.* The hydrostatic pressures in the feed and permeate are equal, but the concentration in one solution (A) is higher than in the other solution (B). Thus, the osmotic pressure in solution (A) is higher than that in solution (B), and water flows from the more dilute solution (B) to the more concentrated solution (A).
- (3) *Osmotic Equilibrium.* The feed and permeate have different concentrations and hydrostatic pressures, but the ΔP and $\Delta \pi$ of the system are equal, which means that in Equation (1), J_w is zero and no flow of water occurs through the membrane.

(4) *Reverse Osmosis*. The feed and permeate have different hydrostatic pressures, but the ΔP across the membrane is larger than that of the difference of osmotic pressure, $\Delta\pi$, acting in the opposite direction. Thus water flows through the membrane from the more concentrated solution (A) to the more dilute solution (B). In this study, only the reverse osmosis separation mode was considered.

(5) *Recycling Process Analysis*

In this study, a recycling process analysis of a single-stage RO system equipped with a thin-film-composite membrane (Filmtec) was selected for plating process (a). On the basis of Equations (2) through (6), it was found that when the feed solution has a TDS of 460 ppm, TSS of zero, a pH of 2 to 10, and a temperature of 25°C, the flux (J_w) ranged from 5.5 to 8.0×10^{-4} cm³/cm².sec, the minimum percent rejection was greater than 95%, the recovery rates were between 90 and 95%, and the TDS in the purified water (permeate) could range from 35 to 80 ppm depending on the applied pressure (range from 1.4 to 5.5 MPa, respectively). A RO that provides a flux of 6.5×10^{-4} cm³/cm².sec with 19 liter/min flow capacity is currently used by this shop.

Ion Exchange

(1) *Water Quality and Ion Exchange Efficiency*

Because the plating process demands a high quality of purified water with conductivity equal to or less than 2 μ -mho/cm, the permeate from a RO must be polished by an ion exchange (IX) unit before returning to the process. Thus an IX system equipped with strong-acid cation and strong-base anion resin beds will be selected for this water recycling process. Since the TDS of the rinsewater process (a) or (b) is normally high (≥ 500 ppm), use IX alone will require frequent resin regeneration or generate high volume of contaminated resins. A combination of OR and IX units is thus needed.

Ion exchange is a chemical reaction between a solid resin and wastewater in which the positive and negative ions in the liquid exchange locations with the ones on the surface of the solid. In aqueous solution, fixed ions within the exchanger and mobile ions in both the resin and the solution are normally hydrated (see Equation 1). The resin prefers the hydrated ion of smallest radius. In general, multivalent hydrated ions are smaller in size than ions of lower valence. Therefore, the adsorption of ions with higher valence to resins is favored.

When a dilute solute of electrolytes passes through an IX unit, substantial concentration differences between resin and solution phases exist. These concentration gradients cause diffusion of ions into and out of the resin. The diffusion of ions tends to build up an electric potential difference between resins and the solution. This potential difference, the Donnan potential, will draw counter-ions back into the respective phases. For example, cations and anions will be drawn into a negatively charged resin and a positively charged solution phases, respectively. Thus an equilibrium condition will be established in which the diffusion of ions is balanced by the existence of the Donnan potential [9].

(2) *Selection of Resins*

The performance of IX system relies on choosing the proper resin type, operating conditions, pH control, low concentration of metal ions in the feed solution, suitable flow rate, and system design. Several factors influence the selection of a resin type: pretreatment requirements, type and concentration of constituents present in the feed, the accumulation rate of metal salt in the bath, operating time, and the ease of resin regeneration. Resin selectivity depends on ionic charge and size. The force with which an ion is attracted is proportional to its ionic charge; therefore, the counter ion of higher valence is more strongly attracted into the resin. With regard to ionic size, ions of smaller radius are preferentially adsorbed, because smaller ions can most readily enter the matrix of the resin and react with its functional group.

Exchanger categories include strong and weak cation, strong and weak anion, and chelating ion exchangers. Strong-acid cation resins derive their functionality from sulfonic acid groups (HSO_3^-). The capacity of strong-acid cation exchangers is independent of the solution pH. Weak-acid cation resins derive their exchange ability from a carboxylic group (COOH). Normally, weak cation resins can be used for solutions containing low concentrations of metal ions in a proper pH range. For high concentration solutions, a strong cation/anion exchanger may be preferred. Weak-acid cation exchangers demonstrate limited capacity below a pH of 6 [18]. This is due to the dissociated nature of these resin types. Both strong-acid and weak-acid cation resins have either hydrogen or sodium form. However, different forms of resins require different regeneration agents.

Strong-base anion resins derive their exchange activity from quaternary ammonium functional groups. Two types of quaternary ammonium groups, such as one has three methyl groups and another has only two, are used. Both of them are highly ionized and can be used over a wide pH range to remove ionized acids. Weak-base anion resins functionality originates in amine groups (NH_2 , NHR' , or NR'_2). They are strongly influenced by solution pH. Both strong-base and weak-base anion resins have either hydroxide or chloride form.

One study [18] has shown the experimental results of using a chelating ion exchanger to treat printed circuit board wastes containing complexed copper from alkaline rinse dumps, electroless copper dumps, and different rinse effluents. The copper concentration in the mixture ranges from 2 to 65 mg/L. The results show that the higher the copper concentration of the influent, the poorer the separation result. They also found that as the flow rate increases, an early breakthrough of copper from the column is observed.

Gold et al. [19] conducted a series of experiments to treat the contaminated electroless and electrolytic nickel plating baths with different chelated resins. For treating an electroless nickel bath, their results show that the Amberlite IRC-718 resin is more selective to copper (94%) than nickel and is relatively selective to zinc and lead (50%). With Duolite ES-467 resin, the resin shows excellent lead and zinc removal (89%). The copper removal is about 75%. For both resins, the removal of iron and chromium (VI) was not significant. Experiments of treating an electrolytic nickel plating bath show that IRC-718 resin removes 70% of copper

and iron, 50% of chromium (VI), lead, and cadmium, 15% of zinc, and only 10% of nickel. ES-467 resin shows a higher selectivity for contaminated metals relative to nickel than did IRC-718. Lead and iron are almost completely removed; over 85% of zinc, copper, and chromium are removed. From these experiments, it was found that neither these two resins can effectively treat waste streams containing combined heavy metal ions.

Holl [20] examined the treatment of wastewater containing metal-ligand complexes with anion exchange columns. It was found that in principle, anionic heavy metal complexes, such as copper-EDTA or copper-tartrate, can be effectively removed from wastewater by means of anion exchangers, such as Amberlite IRA 958 (acrylic strong-base resin), IRA 35 (acrylic weak-base resin), or Lewatit MP 600 (styrene-based resin). Since polymers containing nitrogen atoms as electron donors can form coordination compounds with heavy metals, polyacrylic or polystyrene acid can form complexes with copper and therefore allow its effective removal.

A similar study [21] to the previous one was also performed with anion resins. It found that simultaneous removal of lead- and cadmium-EDTA complexes can be achieved with Amberlite IRA-68 (a weak-base acrylic resin) or Amberlite IRA-400 (a strong-base polystyrene resin) resins. However, their results also indicated that the presence of other anionic ions in water greatly decreased the resin capacity for complexed species.

(3) Resin Regeneration and Regenerant Treatment

There are several drawbacks to the IX separation technique:

- (1) process streams need pretreatment, filtration, and pH control;
- (2) only dilute waste streams are suitable to be treated with IX systems;
- (3) the spent resin must be regenerated before reusing the resin, but the efficiency of regeneration is limited by the characteristics of resin, metal ions and regenerants; and
- (4) the final treatment of the exhausted regenerant presents a problem.

Regenerating the saturated resin and recovering the spent

regenerant solution are also important for using ion exchangers. There is one major disadvantage to a high degree of selectivity in an exchange reaction: the reluctance of the resin to release the ion during regeneration. The highly specific chelating resin requires much more regenerant than that required for regenerating weak-acid cation resins. The weak-acid cation and weak-base anion resins demonstrate the relative ease with which it is regenerated. Examples of resin regeneration agents are listed in Table 4.

The conventional electrowinning technology has been applied to replenish the spent regenerant. Other replenishing methods, such as evaporation, precipitation, or electro-dialysis, have also been evaluated. A series of experiments was performed to investigate the application of the chelating agents as regenerant of a strong-acid cation resin and to select a method of recovery of the chelating agent [22]. Their results showed that the regeneration effectiveness for a copper, zinc, and nickel exhausted exchanger (Dowex 50W-X10 resin) with EDTA, NTA, and CIT and with pH between 6 and 9 is in the order copper > zinc > nickel. Regeneration effectiveness of EDTA and CIT are better than NTA. It was found that an electro-dialysis was efficient in recovering metal and chelating agent from spent regenerant.

(4) Recycling Process Analysis

In this study, because the plating process demands a high quality of purified water with conductivity less than 3 μ -mho/cm, an IX system equipped with strong-acid cation resin (Lewatit SP 112 or Amberlite 200) and strong-base anion resin (Lewatit M 500 or Amberlite IRA-900) beds was selected for providing de-ionized water to a rinsewater recycling process. However, a chelating resin (Ionac SR-5 or equivalent) and a strong-base anion resin (Amberlite IRA-400, -900, or Lewatit M 500) will also be tested to treat wastewater containing anionic EDTA-copper complexes. The characteristics and operating conditions of several resins are listed in Table 4.

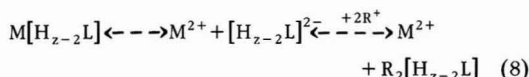
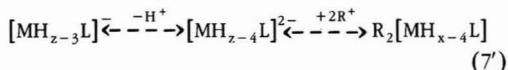
In order to optimize the operating conditions and reduce the regeneration frequency, the TDS concentration of the feed waste stream will be limited below 50 ppm. This requirement can be achieved by properly operating the RO unit. The ratio of wastewater volume to resin volume in the

TABLE 4. Operating Conditions and Characteristics of Selected Resins

Feature	Lewatit SP 112	Lewatit M 500	Amberlite IRA 400	Ionac SR 5
Ionic form	Sodium	Chloride	Chloride	Sodium
Functional group	Sulfuric acid	Quaternary amine	Quaternary ammonium	Iminoacetic acid
Matrix	Polystyrene	Polystyrene	Divinylbenzene	Styrene/Divinylbenzene
pH range (stability)	0-14	0-14	No limit	1-14
Water retention (wt%)	45-50	45-50	42-48	45-50
Minimum depth (m)	0.76	0.76	0.61	0.76
Service flow (1/hr/l)	128	128	38	32
Backwash flow (m/hr)	19	18	19	5
Regenerant	H ₂ SO ₄ (4%) or HCl (5%)	NaOH (4%)	NaOH (4%)	H ₂ SO ₄ (10%) or HCl (8%)
Regeneration time (hr)	1	1	1	1

resin columns will be selected in the range of 0.25 to 0.50 m³/min-m³. Higher rates will not be considered because they usually result in higher leakage. An IX unit with a 19 liter/min flow capacity is used for this plating process.

The dissociation-sorption reactions of ligand-metal complexes or ligand in the anionic resin bed will be examined. Three examples are presented below.



where R represents the exchange site of anionic resins. Equations (7), (7'), and (8) are competing reactions. The former two are preferred, but the later one is not because the presence of free metal ions in the treated solution. Our precipitation analysis described above indicated that the solution pH influences the dissociation-formation reactions of metal-ligand complexes and ligands (i.e., H_zL, [H_{z-2}L]²⁻, etc.). Thus the solution pH will also influence these three reactions and consequently the metal-ligand removal efficiency.

Wastewater treated by a mixed resin bed was also considered. The mixed resin bed can provide ultra-pure water with nearly 0.02 μ-mho/cm conductivity (or 16–18 megaohm-cm resistivity). Since the plating process does not need such high quality deionized water and the regeneration of a mixed resin bed is more difficult than that of an acid or base resin bed, the mixed resin bed was not selected for this plating process. Regeneration of the exhausted acid and base resins will be based upon the general guidelines listed in Table 4. In this study, the spent regenerant will be replenished by using an existing electrolytic cell or electrowinning unit of this plating process.

SUMMARY

Both RO and IX systems are feasible to treat and recycle rinsewater. However, since the TDS in the spent rinsewater is normally high (≥ 500 ppm), it is not suitable to use IX alone to treat wastewater generated from process (a). Thus, a combination of RO and IX is preferred. A RO can produce a permeate (purified water) with 35–80 mg/l TDS. The permeate from the RO will be further polished by an IX.

The RO/IX system can provide and recycle deionized water with less than 3 μ-mho/cm conductivity. This system will generate less than 7,000 liters/year rejected solution, which is less than 10% of the total waste stream usually generated by plating process (a).

This study also evaluated the feasibility of the overall process of regeneration, recovery, and reuse of the resin regenerant. Electrowinning is selected as a suitable method of recovery and reuse for the acid regenerant.

Because agitation, high current, and large surface area cathodes are needed, EW is not usually considered to treat solutions with metal ions concentration less than 100 mg/l.

Thus, a treatment system with an EW (for metal ions concentrations greater than 100 mg/l) and followed by an IX (for TDS less than 150 mg/l) was evaluated. The EW/IX system is also feasible to treat and recycle rinsewater back to the process. However, its annual operating cost (\$10,000) will be higher than that of the RO/IX system (\$6,000).

After optimizing its process conditions and operation procedures, the performance of the existing precipitation system has been greatly improved and the treated wastewater can meet the discharge limit. However, the treated wastewater is not recyclable because its TDS is high (~ 3,000 ppm). The annual operating cost, including permitting and monitoring costs, is also high (\$12,000).

Although the precipitation method is widely used in industries, there are major limitations to this method: (i) the removal of metal ions of combined metal wastewaters will not be effective because the minimum solubilities of different metal salts occur at different pH conditions; (ii) the presence of chelating agent in the wastewater has an adverse effect on metal removal; (iii) little metal removal occurs for pH less than 6; (iv) the sludge quantity is substantial; and (v) the treated water is not recyclable.

A deionized rinsewater recycling process was also designed for plating process (b). It can process approximately 80 liters/min of used rinsewater. With these two rinsewater recycling systems for plating processes (a) and (b), LBNL expects to reduce and reuse approximately 7.5 millions liters of wastewater annually (33% of total wastewater).

LITERATURE CITED

1. SB-14 Hazardous Waste Source Reduction and Management Review Plan, Lawrence Berkeley National Laboratory, (1995).
2. **Chang, L. Y.**, A Waste Minimization Study of a Chelated Copper Complex in Wastewater-Treatability and Process Analysis, *Waste Management*, Vol. **15**, No. 3, pp. 209–20 (1995).
3. **Stumm, W., and J. J. Morgan**, Aquatic Chemistry, pp. 323–86, John Wiley & Sons, (1981).
4. **Martell, A. E.**, Principles of Complex Formation, in Organic Compounds in Aquatic Environments, ed. by S.D. Faust & J. V. Hunter, pp. 239–63, Marcel Dekker, (1971).
5. **Weber, J. H.**, Metal Ion Speciation Studies in Presence of Humic Materials, pp. 315–31, in Aquatic Terrestrial Humic Materials, Ed. by R. F. Christman and E. T. Gjessing, Ann Arbor Science, (1983).
6. **Benedetti, M. F., C. J. Milne, D. G. Kinniburgh, W. H. Van Riemsdijk, and L. K. Koopal**, Metal Ion Binding to Humic Substances: Application of the Non-Ideal Competitive Adsorption Model, *Environ. Sci. Technol.*, Vol. **29**, pp. 446–57, (1995).
7. **Smith, R. M. and A. E. Martell**, Critical Stability Constants, Vol. 1, Plenum Press, (1974), cited in Chelating Agents, Kirk-Othmer's Encyclopedia of Chemical Technology, Vol. **5**, John Wiley & Sons, (1979).
8. **Hering, J. G. and F. M. M. Morel**, Kinetics of Trace Metal Complexation: Ligand-Exchange Reactions, *Environ. Sci. Technol.*, Vol. **24**, pp. 242–52, (1990).
9. **Weber, Walter J., Jr.**, Physicochemical Processes for Water Quality Control, Wiley-Interscience, (1972).

10. **Clark, M. M. and R. M. Srivastava**, Mixing and Aluminum Precipitation, *Environ. Sci. Technol.*, Vol. **27**, pp. 2181-89, (1993).
11. **Chang, L.-Y. and B. McCoy**, Waste Minimization for Printed Circuit Board Manufacture, Hazardous Waste & Hazardous Materials, Vol. **7**, p. 293, (1990).
12. **Chang, L.-Y. and B. McCoy**, Alternative Waste Minimization Analyses for the Printed Circuit Board Industry: Examples for Small and Large Manufacturers, *Environmental Progress*, Vol. **10**, p. 110 (1991).
13. **Farekh, B. S.**, Reverse Osmosis Technology: Application for High-Purity-Water Production, Marcel Dekker, (1988).
14. **Huang, Y.-C. and S. S. Koseoglu**, Separation of Heavy Metals from Industrial Waste Streams by Membrane Separation Technology, *Waste Management*, Vol. **13**, p. 481, (1993).
15. **Buckley, C. A., K. Treffry-Goatley, M. J. Simpson, A. L. Bindoff, and G. R. Groves**, Pretreatment, Fouling, and Cleaning in the Membrane Processing of Industrial Effluents, in Reverse Osmosis and Ultrafiltration, pp. 429-37, Ed. by S. Sourirajan and T. Matsuura, American Chemical Society, (1985).
16. **Bhattacharyya, D., M. E. Williams, R. J. Ray, and S. B. McCray**, Design and Selected Application (Reverse Osmosis), in Membrane Handbook, pp. 281-354, Ed. by W. S. W. Ho and K. K. Sirkar, van Nostrand Reinhold, (1992).
17. **F. P. Reinhard** of EG&G Environmental, Minnesota, May, (1995), private communication.
18. **Karr, S., D. M. Buckley, and F. A. Steward**, Ion Exchange for Metal Recovery: A Discussion of Trade-Offs, pp. 60-66, Plating and Surface Finishing, (April, 1986).
19. **Gold, H., et al.**, Purifying Plating Baths by Chelate Ion Exchange, in Metal Speciation, Separation, and Recovery, ed. J. W. Patterson & R. Passino, Lewis Publishers, (1987).
20. **Holl, W. H.**, Unusual Column Behavior of Heavy Metal Complexes on Anion Exchange Columns, in Ion Exchange Processes Advances and Applications, ed. by Dyer, A., M. J. Hudson, and P. A. Williams, Royal Society of Chemistry, (1993).
21. **Dudzinska, M. R., and L. Pawlowski**, Anion Exchange of Heavy Metal-EDTA Complexes, Ion Exchange Processes Advances and Applications, ed. by Dyer, A., M. J. Hudson, and P. A. Williams, Royal Society of Chemistry, (1993).
22. **Patterson, J. W., and R. Passino**, Metals Speciation, Separation, and Recovery, pp. 571-85, Lewis Publishers, (1987).

Development of a Wastewater Treatment Process: Reductive Dehalogenation of Chlorinated Hydrocarbons by Metals

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A low-energy dechlorination technique has been applied to the detoxification of chlorinated hydrocarbons (CHCs) in aqueous solution. This alternative to biological or physico-chemical decomposition methods achieves reduction by means of metal particles or copper-activated metal particles (Mg, Fe, Al, Zn).

The paper presents data from two pilot studies, covering fundamental process design aspects. Experimental investigations of pilot study 1 were conducted in a laboratory-scale fixed bed reactor. In weak acidic or neutral medium (pH-range 4–7) proper process application resulted in very rapid removal of hexachlorocyclohexane concentration (γ -BHC, lindane) from model wastewaters with up to 99.3% efficiency. During the course of reaction the main products formed are chloride and benzene, the by-product being small amounts of chlorobenzene. After employing different metals in the dechlorination reaction zinc proved to be the optimum reducing agent since it achieved the best space-time yield. Pilot study 2 dealt with a couple of screening reactions of various CHCs with zinc as the reducing agent, which were performed in the batch mode. Even volatile CHCs (chloroform, 1,1,1-trichloroethane) could be completely dechlorinated by forming the corresponding hydrocarbons (methane; ethane and ethene respectively). Pseudo-first order rate constants (k , s^{-1}) were determined to assess substrate reactivity with respect to possible process applications. Process design aspects, advantages and limitations are discussed.

INTRODUCTION

Chlorinated organics released from industrial, commercial and agricultural sources enter the aquatic environment as persistent pesticides, pharmaceuticals, solvents, dielectric fluids etc. Their extensive use over several decades and their resistance to degradation has led to their ubiquitous presence in various ecosystems. Consequently, the development of new processes for the effective removal of toxic pollutants from the environment has once again focused attention on dechlorination reactions [1–2].

Conventional waste water treatment processes are usually based on incineration [3] or other chemical methods, such as wet oxidation [4], ozonation [5], hydrodechlorina-

tion [6] and alkali metal-based reduction [7, 8]. In addition, physico-chemical and biological processes have been developed. Considering each of these disposal methods, certain process limitations have to be faced. For example, energy consumptive incineration generates corrosive HCl, later requiring neutralisation, or leads to the formation of more toxic oxygenated derivatives (polychlorinated dibenzodioxins and dibenzofurans) [9, 10]. Physical processes, based on extraction, stripping and/or adsorption on activated carbon remove pollutants efficiently without solving the problem of final disposal [11]. Microbial processes have slow degradation rates; a special adaptation of suitable microorganisms is necessary [12].

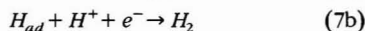
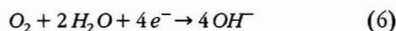
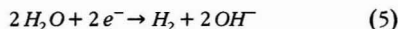
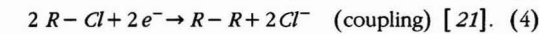
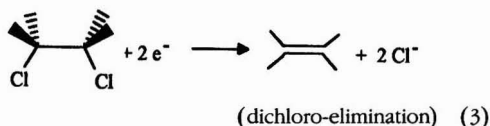
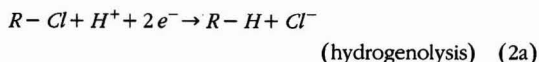
In many cases reductive dechlorination by metal particles is a useful method of solving the problems posed by chlorinated organics. First experimental investigations into employing metals to decompose contaminants were reported by Koch. A cylindrical galvanic cell type, with a set of perforated Mg plates as the cathode and filled with activated carbon particles as the anode, was developed [13]. Reactions of various chlorinated organics with activated metals were described by Sweeny. Electronegative metals like Zn, Al, Fe, Cd or Mg, activated by traces of a catalyst metal such as Cu, Ag, Co, or Ni, served as reducing agents. Sweeny claimed that his process would degrade the full range of chlororganics, including the extremely stable chloroaromatic substrates with a declared 100% degradation efficiency [14, 15]. However, considerable doubts concerning the correctness of these results were raised later on. The apparent transformation of chlorinated biphenyls has been attributed to chromatographic effects in the full scale column reactor rather than to dechlorination [16]. Parameter studies dealing with the physico-chemical background of the corrosion processes involved have been the subject of recent experiments and the starting point for the present study [17, 18]. Two more recent publications deal with a first approach to designing various types of appropriate reaction apparatus for the removal of chlororganic compounds by reductive dehalogenation. The first one describes a filter, whose framework is formed from the porous body of a three-dimensional network and consists of at least one kind of metals Fe, Mn, Mg, Zn, Al and Ti [19]. The second one introduces a kind of fixed bed reactor with an iron-based metal porous body which essentially consists of Fe, but may also contain metals such as Cu, Cr, Ni, Sn or

Zn in order to improve the corrosion resistance of Fe. The apparatus described is run under circular flow and with the addition of H_2O_2 [20]. In the most recent paper, investigations on the sequential reductive dehalogenation of chlorinated methanes by iron metal powder are documented. The study focuses on basic mechanistic aspects, but does not contribute to major progress from a practical point of view, since reaction rates are very low and dechlorination is incomplete [1].

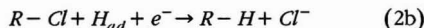
The principle of reductive dechlorination by metals in aqueous solutions can be regarded as an electrochemical corrosion process. The driving force of the reaction is a corrosion reaction, which consists of several partial steps. Anodic metal dissolution:



provides electrons for the reduction, occurring as:



Hydrogen is assumed to develop according to the well known Heyrowski mechanism of hydrogen evolution. This mechanism could involve the reaction of adsorbed hydrogen H_{ad} with CHCs according to:



It is evident that further investigations into mechanisms require an appropriate design of additional experiments.

This paper aims at the development of a basis for the process of reductive dehalogenation of selected chlorinated hydrocarbons by metal particles in wastewater streams. Experiments are performed so that basic information on reactor design and possibilities for upscaling from laboratory to full scale can be obtained. Research investigations were classified into two main studies. Pilot study 1 covered the process development in a laboratory-scale fixed bed reactor by investigating conversion, space-time yields and process parameters for different reducing agents (based on Fe, Mg, Al and predominantly Zn) using lindane (γ -hexachlorocyclohexane) as the model compound.

Pilot study 2 was devoted to screening reactions of various volatile contaminants of environmental concern (e.g., chloroform, 1,1,1-trichloroethane, perchloroethylene, trichloroethylene and chlorobenzene) and zinc as the re-

ducing agent. These reactions were conducted in the batch mode and delivered valuable information on degradation kinetics and thereby perspectives for possible process applications with regard to the chlorinated organic contaminants present in the wastewater. Finally, this study provides an outline on process advantages and limitations and evaluates feasibility of introducing the process into industrial application.

MATERIALS AND METHODS

Reagents

Technical grade iron (iron content: 93–96%) was purchased from Surfatec GmbH. Aluminium (purum, >99%) and magnesium (purum, >99.8%) were purchased from Fluka Feinchemikalien, zinc (>99.9%) was obtained from Grillo Werke AG. The particle size range of the metals used was 0.2–0.4 mm. Either pure metals or metallic couples with copper as the catalyst metal were employed. In a chemical cementation reaction, a metal ion in solution is reduced to the corresponding metal by accepting the required number of electrons. The source of these electrons is the oxidation of a less noble metal, which is referred to as the reducing agent. The cementation of cupric ions from dilute copper sulphate solutions on iron particles is a well known reaction, which has been previously described in the literature. Before use the metal was acid etched by sulphuric acid (5%) in order to remove impurities from the surface. After washing it with water and ethanol the cementation of the copper layer was carried out by moderately stirring the metal particles in an aqueous solution of 1g copper sulphate per 500 g reductant [17], followed by further washing procedures with twice distilled water and ethanol. The metallic couple was filtered and placed in a drying oven at 60°C for 2h.

Analytical grade lindane was obtained from Riedel-de Haen. All other common chemicals (Merck) were at least reagent grade, used without further purification. Solutions were prepared with twice distilled water.

Equipment and Analyses

A solid phase extraction (SPE) device (Baker), including vacuum manifold, vacuum gauge, solvent guide needles and sample collection rack, was used for cleanup procedures of lindane samples. Solid phase extraction cartridges were 3 ml capacity, containing 500 mg of C_{18} sorbent material. Details of cleanup procedures can be found elsewhere [22].

GC-MS experiments were run on a Finnigan MAT ITD 800 ion trap detector mass spectrometer interfaced to a Varian 3300 gas chromatograph, equipped with a CTC A200S Autosampler (Axel Semrau). 1 μ L of a lindane sample extract (solvent: hexane) was injected splitless (1 min) into a 25 m \times 0.25 mm bonded phase FS-SE54 (= DB 5) column with a film thickness of 0.25 μ m (Chromatographie Service). The GC oven temperature was programmed as follows: isothermal at 60°C for 1 min, 60°C to 200°C at 25°/min, 200°C to 250°C at 4°/min [23]. The carrier gas was helium at a flow rate of 1 ml/min.

A 50 m \times 0.32 mm FS-SE 54 column with a film thickness of 0.25 μ m was used for analytical determination of volatile chlorinated compounds. Aqueous samples were

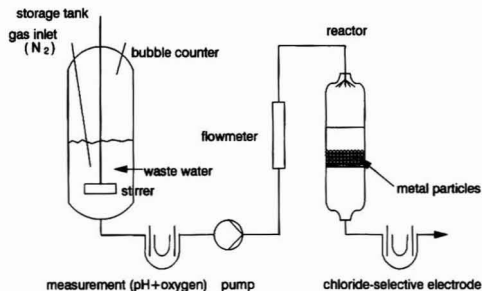


FIGURE 1 Schematic representation of the micropilot plant.

extracted with hexane. Temperature program: 3 min isothermal at 35°C, 35 to 220°C at 4 °/min, 10 min isothermal. Split injection, injection volume 2 μl [24]. Contaminant quantification was based on external standard calibration: the ratio of analyte peak area to external standard peak area was calculated. A multipoint calibration was used, which was fitted by linear regression. Automated library searching enabled peak identification of chromatographic peaks (substrates and decomposition products).

Supplementary compound identification of gaseous dechlorinated products was conducted using GC-FID (VEGA 6300-01, Carlo Erba). A GS-AL 30 m \times 0.53 mm column (PLOT) was used. Sample chromatography was accomplished using the following temperature program: isothermal hold at 80°C for 2 min; temperature increase at 5°/min to 120°C; isothermal hold at 120°C for 5 minutes; temperature increase at 20°/min to 160°C; isothermal hold at 160°C for 3 min.

The introduction of the samples to the GC ($V_{inj} = 100\mu\text{l}$) was carried out in the splitless mode. The carrier gas was hydrogen at a flow rate of 7 ml/min. Compound identifica-

tion was based on retention time according to previously obtained calibration data.

The chloride concentration was measured potentiometrically by a selective chloride ion electrode (Ingold) with an Ag/AgCl reference electrode. 1 M KNO_3 served as intermediate electrolyte in order to avoid chloride contamination problems. The system was calibrated with aqueous solutions of sodium chloride after adjusting of the ionic strength. According to the producer's technical data precision better than ± 0.5 mV corresponding to $\pm 2\%$ of the measured chloride concentration is obtainable. A Perkin-Elmer 100B atomic absorption spectrophotometer was used to analyse for dissolved Fe and Zn.

Before starting the dechlorination experiments, a contaminant adsorption profile was measured without using a reductant. Lindane concentrations in the effluent water stream were determined. By considering these adsorption data, decomposition could be separated from mere adsorption losses caused by possible lindane adsorption to reactor surface or pipe connections.

Pilot Study Descriptions

A schematic representation of the micropilot plant used in pilot study 1 is depicted in Figure 1. The fixed-bed reactor constructed had an internal diameter of 6 cm and a height of 10 cm. This provided an effective bed volume of approx. 0.3 L. A storage tank of 6 L volume was filled with model wastewater. The experimental conditions used are provided in Table 1. To avoid oxygen-induced corrosion, nitrogen was bubbled through a frit into the reaction solution 30 min prior to and throughout the experiment. After passing pH and oxygen measurement units, the solution was pumped into the reactor filled with various reductants. Samples were collected at a sampling port and subsequently analysed by GC/MS. During the experiments, the chloride concentration was continuously monitored by a

TABLE 1 Pilot Study 1: Experimental Conditions for Various Lindane Decomposition Reactions in a Laboratory-Scale Fixed Bed Reactor at 25°C

reductant	Fe/Cu	Al/Cu	Mg/Cu	Zn
initial lindane concentration c_0 / $\mu\text{mol/L}$	13.65	14.1	13.34	8.43
buffer solution	Citrate/NaOH	NaOAc/HOAc	Citrate/NaOH	Citrate/NaOH
volumetric fraction of buffer solution used / %	10	8	10	10
pH value adjusted	5	5	5	6.6
volumetric fraction of carrier solvent (EtOH)/ %	2	3	2	4
reductant mass/g	500	100	100	5
flow rate/L/h	2	0.8	0.8	0.8
electrolyte modification concentration of salt added/mol/L		NH_4F 0.01	NH_4NO_3 0.05	

TABLE 2 Pilot Study 2: Experimental Conditions for Various Volatile Chlorinated Substrates in the Dechlorination Reaction With Zinc in Aqueous Solutions Performed as Batch Experiments at 25°C

	1,1,1-tri-chloroethane	chloroform	perchloro-ethylene	trichloro-ethylene	chlorobenzene
volumetric fraction (%) of buffer solution Citrate/NaOH pH = 5	10	20	20	20	20
reductant mass /g	100	200	200	200	200
initial contaminant concentration / $10^{-3} \text{ mol l}^{-1}$	4.02	2.49	0.78	3.34	1.97

chloride-selective electrode. Process parameters, that were varied in the investigations, were the type of reductant metal, residence time in the reaction zone (determined by m_{red}/w), electrolyte composition and pH value. All experiments were run at room temperature (25°C).

Pilot study 2 experiments were carried out in a 2L three-necked flask equipped with a stirrer. This experiment set-up avoided volatilization losses and permitted identification of gaseous products as well. Solutions for each component were prepared by adding a certain amount of organic toxicant (under the solubility limit) to a volume (1L) of water after purging it with nitrogen for 30 min. The composition of the solutions employed is provided in Table 2. The flask was sealed with a silicone rubber septum cap with a Teflon liner facing towards the reaction vessel. Gaseous samples were withdrawn from the flask using a gastight syringe and subsequently analysed. Reactivity and degradation pathways of the substrates investigated were obtained.

RESULTS AND DISCUSSION

Pilot Study 1

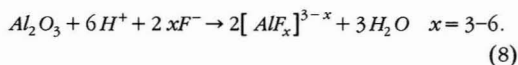
Reductive Lindane Degradation by Fe/Cu

Lindane decomposition by the metallic couple Fe/Cu is shown in Fig. 2. Using 500 g reductant at a flow rate of 2 L/h, a lindane conversion of 99.3% in 40 min) was measured.

Further experiments focused on the influence of residence time (by varying m_{red} and w , given in Table 3) on conversion and space-time yields. The results offer two diverging effects (Figure 3). Of course, conversion improvement is achieved with increasing residence time in the reaction zone, but space-time yields fall similarly. This sharp decrease can be explained in terms of reduced selectivity concerning the dechlorination process. Reaching quantitative lindane conversion, reductant consumption is mainly caused by side reactions. By varying experimental conditions (type of reductant metal, electrolyte composition, pH), in subsequent investigations this relevant selectivity problem was to be optimized.

Reductive Lindane Degradation by Al/Cu

Lindane decomposition was studied, using Al/Cu as the reductant. In this context, the main problem arises from the protective aluminium oxide layer, prohibiting a corrosion process. By introducing fluoride ions into the electrolyte, a change in the ionic and electronic properties of the passive layer can be achieved. Fluoride ions enter the oxide film, removing it by forming water soluble fluoro complexes. Moreover, repassivation of the active metal surface is prevented as well [25, 26]. The reactions can be described as follows:



By providing these experimental conditions (Table 1), an 89% lindane conversion (in 105 min) was obtained (Figure 2). However, the presence of fluoride ions in this concentration range (approx. 190 mg/l) is very troublesome, as existing limits for process wastewaters (20-50 mg/l F^-)

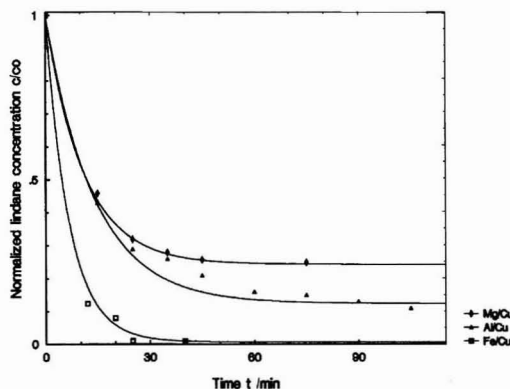


FIGURE 2 Reductive dechlorination of lindane by Fe/Cu, Al/Cu and Mg/Cu, pH = 5; Measured disappearance as a function of time at 25°C. Experimental conditions are given in Table 1.

TABLE 3 Pilot Study 1: Reductive Dechlorination of Lindane by Fe/Cu, pH=5. Conversion C and Space-Time Yield y as Functions of Residence Time.

m_{red}/g	$w/l\ h^{-1}$	m_{red}/w /gh l^{-1}	$y/10^{-3}$ mol $l^{-1}\ h^{-1}$	C %
500	2	250	2.55	99
400	1.66	241	2.82	96
100	0.8	125	2.9	92
100	1.66	60	7.57	79
20	0.8	25	26.3	61

are substantially exceeded. Therefore, aluminium-based investigations were not continued at this point of the study.

Reductive Lindane Degradation by Mg/Cu

By providing suitable experimental conditions (Table 1), a 72% lindane conversion (in 40 min) was achieved (Figure 1). However, during the course of the experiment, Mg turned out to be a less favourable reductant. Though the maximum driving force of the dechlorination reaction was provided, its net effect was the pronounced, strongly exothermic reaction with water.

Reductive Lindane Degradation by Zn/Cu and Zn

At pH = 5 the influence of copper cementation on the lindane degradation by zinc was studied. Contrary to former investigations [17] previous copper cementation is not necessary, since a remarkable increase in the reductant's degrading effect was observed when using pure zinc. Additional investigations supplied further experimental evidence of this tendency. An improvement in reductant activity with decreasing copper contents of the reductant was found.

Using pure zinc at pH = 5, the disappearance of lindane was found to occur very rapidly. Due to this fact residence times could be shortened by using smaller amounts of re-

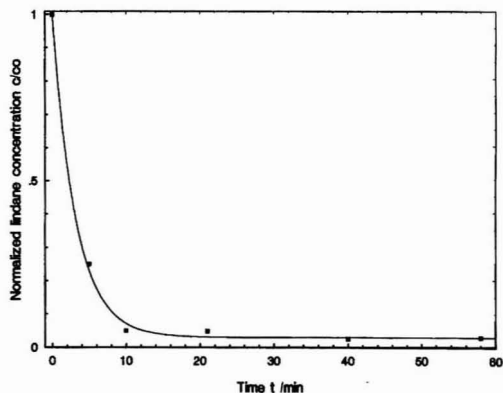


FIGURE 4 Reductive dechlorination of lindane by Zn, pH = 6.6. Measured disappearance as a function of time at 25°C. Experimental conditions are given in Table 1.

ductant without any greater conversion decrease. The pH of the solution was raised in order to reduce zinc concentration in the effluent solution. A 97.4% lindane conversion was obtained within minutes (Figure 4) under experimental conditions given in Table 1. Reductant activity may be reduced by deposition or adsorption processes. Interference with components present in the wastewater or formed in the course of the corrosion process has to be considered. In an 11h experiment under these optimized experimental conditions (Figure 4) reductant activity was studied as a function of time. However at the time of the investigation there was no such decrease in reductant activity.

Influence of the Metal Used on Space-Time Yields

To compare the degrading effect of the various reductants employed in the dechlorination reaction, space-time yields for a given residence time at pH = 5 were calculated. Results are depicted in Figure 4. Logarithmic plots of the space-time yields underline the outstanding role of pure zinc as a reductant. Presumably there are two main reasons for this behaviour. The first is the optimum standard potential in terms of dechlorination selectivity, provided by zinc. A second explanation can be given in terms of suitable porosity of the zinc layers, providing favourable conditions for processes of substrate diffusion to and product effusion from the metal surface. Consequently, subsequent screening reactions, which are described in pilot study 2, were carried out with zinc as it was the most effective reductant.

Metal Concentration in the Effluent Stream

Since dechlorination is achieved by a corrosion process, considerable amounts of metal ions are present in the effluent. Obviously, this concentration of dissolved metal ions should be minimized in terms of a small reductant demand. The water solubility of lindane is 25 μ mol/L (= 7.3 mg/L). Its reductive dechlorination appears to be only a side reaction, since the vast majority of metal consumption is caused by competitive reductive processes {equations (5)–(7)}. But corrosion rate can be influenced by pH value as part of the electrolyte composition. Using pure iron and

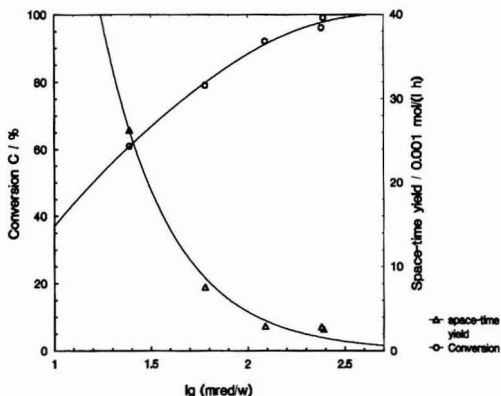


FIGURE 3 Reductive dechlorination of lindane by Fe/Cu, pH = 5; Conversion C and space-time yield y as functions of residence time represented by $\lg(m_{red}/w)$; obtained data according to Table 3.

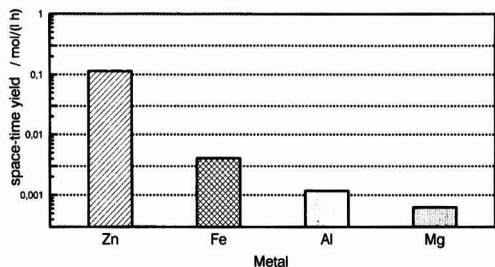


FIGURE 5 Logarithmic plot of space-time yields of different reductants in the lindane dechlorination reaction; Zn, Fe/Cu, Al/Cu, Mg/Cu; pH = 5, $m_{red}/w = 125 \text{ gh l}^{-1}$.

zinc as the reductants, concentrations of dissolved metal ions were measured as a function of pH value under stationary conditions. Data were acquired at a flow rate of 0.8 L/h for the weak acid region ranging from pH 5.0 to 6.6 (Figure 6). A decline of approximately 70% in metal concentration was observed, when the pH was raised by one unit. At pH 6.6 and a reductant mass of 10 g the zinc concentration in solution was reduced to 44 mg/L.

Degradation Products

During the course of the reaction the main products formed were chloride and benzene (95%), the by-product being small amounts of chlorobenzene (5%). Intermediates were not detected. Hence reductive lindane dechlorination can be described by the overall reactions:

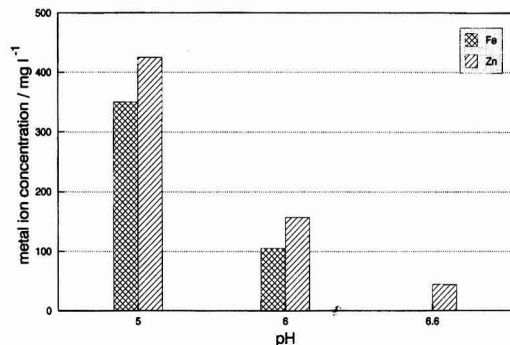
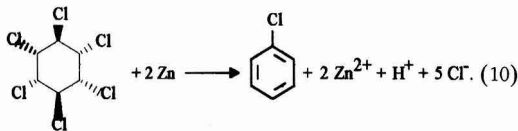
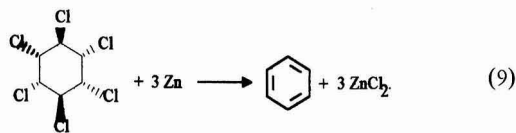


FIGURE 6 Metal ion concentration in the effluent stream. 200 g pure Fe, pH = 5 and pH = 6, 200 g pure Zn, pH = 5 and pH = 6, $w = 0.8 \text{ l/h}$ 10 g pure Zn, pH = 6.6.

Due to their toxicity benzene and chlorobenzene require further treatment subsequently. In this particular case of lindane decomposition the use of a reductive process by metal particles brings about incomplete dechlorination as a chlorinated by-product is formed. It has to be concluded that this process should be regarded as part of a combination of different wastewater treatment techniques. Further general aspects concerning these problems will be addressed at the end of this paper.

Pilot Study 2

Screening Reactions with other Halogenated Hydrocarbons

Since best space-time yields were obtained using zinc as the reductant, screening reactions of several chlororganic substrates of environmental concern with zinc were subjected to further experimental investigations. The extension of possible process applications of reductive dechlorination by zinc was to be examined. The compounds selected were chloroform, 1,1,1-trichloroethane, perchloroethylene, trichloroethylene and chlorobenzene. Reactivity and degradation pathways of the substrates investigated were obtained. The composition of the solutions employed is provided in Table 2.

Kinetic studies were conducted by measuring the rate of chloride release with a chloride selective electrode. These results were confirmed by analysing the liquid phase by GC/MS. Acquired data were fitted to a pseudo-first order reaction model. Rate constants were obtained from the slopes of semilogarithmic plots of $\ln(100-C)$ versus time, C being conversion (%).

Chloroform

Decomposition of chloroform is depicted in Figure 7. After a reaction time of 85 min a 99.4% conversion was obtained. During the course of the reaction 563 mg/L ($8.6 \cdot 10^{-3} \text{ mol/L}$) zinc has been dissolved in the solution. According to reaction stoichiometry, equation (11), 87% of the corroded zinc was used in the dechlorination process.

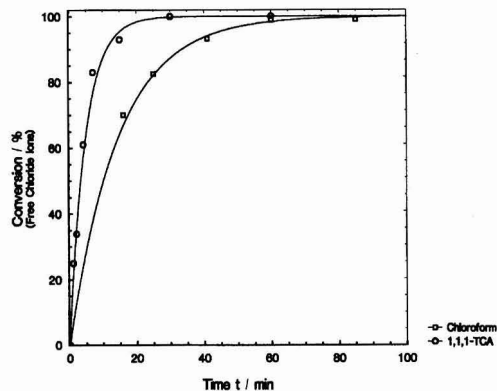
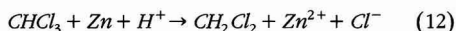


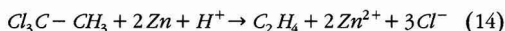
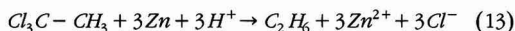
FIGURE 7 Dechlorination of chloroform in aqueous solution, 200 g zinc, pH = 5. Dechlorination of 1,1,1-trichloroethane in aqueous solutions, 100 g zinc, pH = 5. Experimental conditions are given in Table 2.

Methane was the main volatile product detected, traces of methylene chloride (<1%) being the by-product. Chloromethane was not detected. The reductive dechlorination yielding methane and methylene chloride can be described by the overall reactions, eqs. 11 and 12, respectively:



1,1,1-Trichloroethane

As shown in Figure 7, complete dechlorination of 1,1,1-trichloroethane was observed. After 1h reaction time a conversion of 99.6% was achieved. The data for chloride release and trichloroethane removal were consistent. The reaction with zinc showed a rapid transformation into ethane as the main product and small amounts of ethene as the by-product. 1,1-dichloroethane (DCA) was detected as an intermediate. Dechlorination occurs according to the equations:

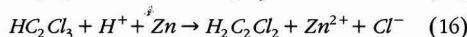
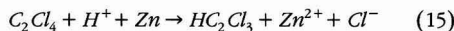


Perchloroethylene (Per)

Qualitative gas phase analysis revealed the concentration-time course of a consecutive reaction with trichloroethylene (Tri) as the intermediate and 3 isomeric dichloroethylenes representing the final stages. Measuring the amount of chloride released as function of time (Figure 8) resulted in quantitative confirmation. Initial chloride formation can be assigned to the first reaction step:

$\text{Per} \xrightarrow{k_1} \text{Tri}$. By evaluating starting kinetics, k_1 was determined. With a reaction time of approximately 2 h, the chloride formation rate decreases significantly as a result of the second, rate-determining step: $\text{Tri} \xrightarrow{k_2} \text{Di}$. As shown in Figure 8, 35% of covalently bonded chlorine was finally

mineralized to chloride after 5 h. Overall reactions can be described as follows:



To investigate the final step of the secondary reaction and to permit determination of the rate constant k_2 , dechlorination of trichloroethylene was studied separately.

Trichloroethylene

The dechlorination of trichloroethylene is depicted in Figure 8. As anticipated, the formation of dichloroethylene was observed. When establishing reaction kinetics, the reduction of trichloroethylene was found to occur ten times slower than that of perchloroethylene. After 4h a conversion of 7.1% was obtained with approximately only 5% of the dissolved zinc being used for the dechlorination reaction.

Chlorobenzene

Chlorobenzene did not undergo reductive dechlorination under these experimental conditions. After 4h reaction time chloride could not be detected.

Kinetic Treatment

The kinetics applied are demonstrated by regarding the dechlorination reaction of chloroform. The rate law was established, assuming the reaction was first order with respect to chloroform concentration [CF] and the concentration of active sites on the solid's surface, [SC], according to the equation:

$$\frac{d[\text{CF}]}{dt} = -k_1 \cdot [\text{CF}] \cdot [\text{SC}] \quad (17)$$

The hypothesis, that [SC] remains constant during the course of the reaction, yields a simplified pseudo-first order rate law:

$$\frac{d[\text{CF}]}{dt} = -k_{\text{obs}} \cdot [\text{CF}]; \quad k_{\text{obs}} = k_1 \cdot [\text{SC}] \quad (18)$$

Integration leads to

$$\frac{[\text{CF}]}{[\text{CF}]_0} = \exp(-k_{\text{obs}} \cdot t) \quad (19)$$

Conversion C is given by equation 20:

$$C = \frac{[\text{CF}]_0 - [\text{CF}]}{[\text{CF}]_0} = 1 - \frac{[\text{CF}]}{[\text{CF}]_0} = 1 - \exp(-k_{\text{obs}} \cdot t) \quad (20)$$

According to reaction stoichiometry {equation (11)} conversion C can be written as a function of the amount of chloride released:

$$C = 1 - \left(1 - \frac{[\text{Cl}^-]}{3 \cdot [\text{CF}]_0}\right) = \frac{[\text{Cl}^-]}{3 \cdot [\text{CF}]_0} = \frac{[\text{Cl}^-]}{[\text{Cl}^-]_{\text{max}}} \quad (21)$$

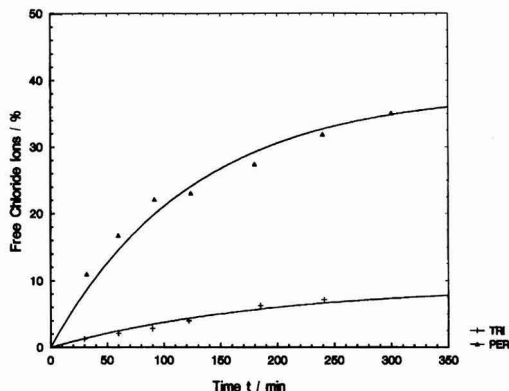


FIGURE 8 Dechlorination of Per and Tri in aqueous solution; 200 g zinc, pH = 5. Experimental conditions are given in Table 2.

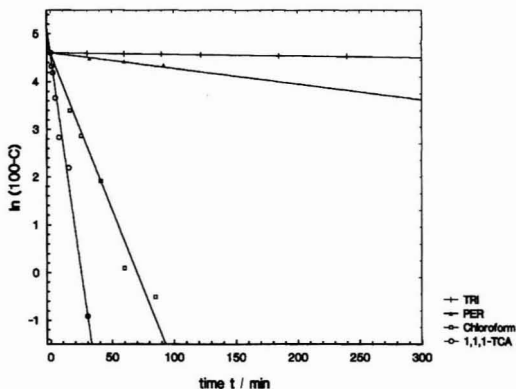


FIGURE 9 First-order kinetic model fits for data from aqueous solutions of some short-chained CHCs with 200 g zinc at 25°C. Semilogarithmic plots of $\ln(100 - C)$ vs. reduction time.

By combining the latter equations (21 & 22), an expression for an appropriate plot can be derived:

$$\ln(1 - C) = -k_{obs} \cdot t \quad (22)$$

or using percentage values:

$$\ln(100 - C) = -k_{obs} \cdot t$$

Consequently, a plot of $\ln(100 - C)$ vs t should yield a straight line, with k_{obs} being the slope.

Kinetic results are displayed in Figure 9. Rate constants (Table 4) vary over several orders of magnitude. However, these values represent only relative reactivities of the substrate investigated, as a strong impact of the water chemistry (wastewater composition, presence of dissolved inorganic or organic compounds) on degradation kinetics was observed. Chloroform and 1,1,1-trichloroethane could be completely dechlorinated by forming the corresponding hydrocarbons within an acceptable reaction time. Concerning aliphatic substrates with chlorine substituents bonded to unsaturated carbon atoms, insufficient reactivity has been recorded. In this case reduced effectiveness of the reductant utilised is the result.

Upscaling Considerations

To design fluid/solid reactions process engineering makes use of tubular flow reactors. Furthermore, selection of an appropriate reactor type depends on kinetics, stoichiometry, reaction heat and mass transfer. The very low concentration range of the toxicants to be converted plays a crucial role in further considerations. There is a small stoichiometrical reductant demand, which is present in excess. Therefore, pseudo-first order kinetics are applied. Moreover, the actually non-catalytic system can be regarded as a heterogeneously catalysed reaction. In this case the most common reactor type used is a fixed-bed reactor. Though, the dechlorination reaction is substantially exothermic, the low toxicant concentration range allows isothermal treatment as well. Consequently, reactor design

TABLE 4 Rate Constants for Dechlorination of Some Short-Chained Chlorinated Organics with 200 g Zinc at 25°C, Obtained by Linear Regression from Pseudo-First Order Model Fits

Compound	k (s^{-1})	R^2
1,1,1-trichloroethane*	$3.05 \cdot 10^{-3}$	0.989
chloroform*	$1.09 \cdot 10^{-3}$	0.991
perchloroethylene +	$5.44 \cdot 10^{-5}$	0.989
trichloroethylene +	$5.5 \cdot 10^{-6}$	0.994

*: complete dechlorination; +: release of one chloride ion)

focuses on mass transfer problems. Questions of heat removal can be ignored.

A suitable pH range for the process can be found in the weak acid region (pH = 4–7). A lower limit arises from the undesirable stripping of volatile compounds due to parallel hydrogen evolution [17, 27]. When raising the pH value in terms of lower metal consumption, the formation of corrosion inhibiting layers (hydroxides and oxide hydrates) must be taken into account. According to dechlorination stoichiometry (equation (23))



there is an equimolar zinc demand for liberation of one mole chloride ions. In other words, typical wastewaters with AOX values in the mg/L (mmol/L) range are expected to contain at least equal zinc concentrations in the effluent stream. The amount of zinc required for reductive dehalogenation based on a demand of two electrons per mole chloride released is given by equation (24):

$$c_{Zn^{2+}} = \frac{AOX \cdot M(Zn)}{M(Cl)} \cdot \frac{100}{S} \quad (24)$$

($c_{Zn^{2+}}$: effluent zinc concentration in g/L; S : selectivity in %; AOX-value in g/L; M : molar masses of zinc and chlorine respectively in g/mol). Since effluent zinc concentration is inversely proportional to selectivity the stoichiometrically required zinc demand is likely to be increased by competitive cathodic steps (equations (5–7)). Selectivity itself depends on degradation kinetics and solubility of the substrate. As a rule, it can be stated that observed selectivities with regard to the dechlorination reaction decreased as reaction time increased, approaching complete conversion. In any case, an additional process of zinc removal (e.g. electrochemical deposition; precipitation or ion exchange) must be established to meet current effluent standards (German limit for discharge wastewaters: 2 mg/L). However, the production of heavy metals in the fluid stream due to the dehalogenation reactions must be regarded as a major disadvantage of the process.

The exposure time of the reducing agent is limited by the rate of anodic metal dissolution, since there is no decrease in reductant activity in the experiments performed. However, disturbing interferences with substances in a complex, multicomponent wastewater cannot yet be excluded in all cases.

CONCLUSIONS

After employing different metals in the lindane decomposition reaction, zinc proved to be the most effective reducing agent, since it achieved the best space-time yields. Contrary to former investigations [17], previous reductant pretreatment with a catalyst metal (Cu) does not increase the rate of lindane degradation. Potential process applications are so far restricted to lindane, 1,1,1-trichloroethane and chloroform, being completely dechlorinated to benzene, ethane and methane respectively. Limitations arise from substrate reactivity (compounds with chlorine substituents in vinylous or phenylogous bonding situations showed poor reactivity) and the undesirable transfer of zinc into wastewater, which requires further treatment to meet current effluent standards. In the light of these aspects the possible application of reductive dehalogenation by metal particles appears to be meaningful only in combination with other wastewater treatment stages. The process advantages of reductive dechlorination by metals in aqueous solution are its simple process technology, the inexpensive reducing agent and its low energy consumption. Contrary to adsorption processes, there is no enrichment, but complete degradation of the toxicants.

ACKNOWLEDGEMENT

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NOTATION

AOX = adsorbable organic halogen, mg/L
 γ - BHC = γ -hexachlorocyclohexane, lindane
 c = toxicant concentration, mol/L
 c_0 = initial toxicant concentration, mol/L
 C = conversion, %
[CF] = chloroform concentration, mol/L
[Cl⁻] = chloride concentration, mol/L
CHC = chlorinated hydrocarbon
DCA = 1,1-dichloroethane
DI = dichloroethylene
FID = flame ionisation detector
 k_{obs} = observed pseudo-first order rate constant, s⁻¹
 m_{red} = reductant mass, g
[SC] = concentration of active sites on the surface, m⁻²
TCA = 1,1,1-trichloroethane; methylchloroform
TRI = trichloroethylene
 V_{inj} = injection volume, μ L
 w = flow rate, L · h⁻¹
 y = space-time yield, mol · L⁻¹ · h⁻¹
 v_i = stoichiometrical coefficient of species i

LITERATURE CITED

1. **Matheson, L. J., and P. G. Tratnyek**, "Reductive Dehalogenation of Chlorinated Methanes by Iron Metal," *Environ. Sci. Technol.*, **28**(11), pp. 2045-2053 (Nov. 1994).

2. **Gilham, R. W., and S. F. O'Hannesin**, "Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron," *Ground Water*, **32**(6), pp. 958-967 (1994).
3. **Santolero, J.**, "Incinerator Technology Overview," *Proc. SPIE-Int. Soc. Opt. Eng. 1434* (Environ. Sens. Combust. Diagn), 2-13 (1991).
4. **Jacob, A.**, "Oxidation Process Tackles Organic Waste," *Chem. Engr. (Rugby-UK)*, **508**, p. 16 (Nov. 28, 1991).
5. **Masten, S. J., and S. H. R. Davies**, "The Use of Ozonation to Degrade Organic Contaminants in Wastewater," *Environ. Sci. Technol.*, **28**(4), pp. 181A-185A (Apr. 1994).
6. **Duebelbeis, D., et al.**, "Application of a Two-dimensional Reaction Chromatography System for Confirmatory Analysis of Chlordane Constituents in Environmental Samples," *Chemosphere*, **20**(10-12), pp. 1401-1408 (1990).
7. **Wentz, J. A., and M. L. Taylor**, "APEG Treatment Process and Results for Chemically Degrading PCBs, PCDDs and Pesticides in Contaminated Soil," *Proc. of National Conference of Hazardous Wastes and Hazardous Materials 7th*, pp. 392-396 (1990).
8. **Hawari, J. A., and R. Samson**, "Process for the Reductive Dehalogenation of Polyhaloaromatics," *US-Pat. 4.950.833*; 21. Aug. 1990; Appl. No 413942.
9. **Olie, K., et al.**, "Formation and Fate of PCDD and PCDF from Combustion Processes," *Chemosphere*, **12** (415), pp. 627-636 (1983).
10. **Dickson, L. C., et al.**, "Quantitative Comparison of de Novo and Precursor Formation of Polychlorinated Dibenzo-p-dioxins under Simulated Municipal Solid Waste Incinerator Postcombustion Conditions," *Environ. Sci. Technol.*, **26**(9), pp. 1822-1828 (Sep. 1992).
11. **Azko BV; Arnhem, Netherlands**, "Porous Plastic Removes Waterborne Hydrocarbon Contaminants," *Chem. Eng. (Int. Ed.)*, **101**, p. 23 (Apr. 1994).
12. **De Bruin, Wil P., et al.**, "Complete Biological Reductive Transformation of Tetrachloroethene to Ethane," *Appl. Environ. Microbiol.*, **58**(6), pp. 1996-2000 (Jun. 1992).
13. **Koch, R.**, "Galvanic Action Water Purifier," *U.S.-Pat. 3 392 102-A* (1968).
14. **Sweeny, K. H., and J. R. Fischer**, "Decomposition of Halogenated Organic Compounds Using Metallic Couples," *US-Pat. 3 737 384* (1973).
15. **Sweeny, K. H.**, "The Reductive Treatment of Industrial Wastewaters: I. Process Description, II Process Applications," *AIChE Symposium Series Water* 1980, **209**, p. 77 (1981).
16. **Erickson, M. D., and E. D. Estes**, "Evaluation of Chlorinated Hydrocarbon Reduction Technology," *U.S. Environmental Protection Agency: Research Triangle Park, NC 1978; Task Final Report; EPA-600/2-78-059*. (Quotation referring to [1]).
17. **Bachmann, T., Vermes I., and E. Heitz**, "Abbau umweltbelastender halogenierter Kohlenwasserstoffe mit Metallen," *Dechema Monographie*, **124**, pp. 221-239 (1991).
18. **Heitz, E., Schlimm, C., and T. Bachmann**, "Außenstromloses elektrochemisches Verfahren zum Abbau von Halogenkohlen wasserstoffen in Wässern," *D.B.P. P 44 07 057.8* (1994), *Eingang: 03.03.1994*.
19. **Kengo Seeno**, "Sewage Treatment," *JP 3-106 496(A)*, *Patent Abstracts of Japan*, C-853, Vol. 15, p. 293 (1991).

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20. **Yozo Takemura**, "Method and Apparatus for Treating Water Containing Organochlorine Compounds," JP 4-100593(A), *Patent Abstracts of Japan*, C-965, Vol. 16, No. 338 (1992).
 21. **Vogel, T. M., Criddle, C. S., and P. L. McCarty**, "Transformations of Halogenated Aliphatic Compounds," *Environ. Sci. Technol.*, **21** (8), pp. 722-736 (Aug. 1987).
 22. **Torreti, L., et al.**, "Determination of Organochlorine Pesticide Residues by Solid Phase Extraction and Dual Column HRGC," *J. High Res. Chromator.*, **15**(2), pp. 99-101 (Feb. 1992).
 23. **Hsu, Jong P., et al.**, "Fast Turnaround Multiresidue Screen for Pesticides in Produce," *J. Assoc. Off. Anal. Chem.*, **74**(5), pp. 886-92 (May 1991).
 24. **Normenausschuß Wasserwesen (NAW) im Deutschen Institut für Normung e.V.**, "Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung Bestimmung von leichtflüchtigen Halogenkohlenwasserstoffen (LHKW) (F4)," *DIN 38 407 Teil 4, Mai 1988*.
 25. **Abd Rabbo, M. F., et al.**, "A Study of Conversion Coating Development on Aluminium in Chromate/Fluoride Solutions Using Secondary Ion Mass Spectrometry," *Corrosion Sci.*, **18**, pp. 117-123 (1978).
 26. **Valand, T., and G. Nilsson**, "The Influence of F⁻ Ions on the Electrochemical Reactions on Oxide-Covered Al," *Corrosion Sci.*, **17**, pp. 449-459 (1977).
 27. **Gemmler, A., et al.**, "Mit Elektrochemie gegen Chlorkohlenwasserstoffe," *Metalloberfläche*, **44**(3), pp. 109-116 (Mar. 1990).

Analysis of Non-Isothermal, Wet Oxidation Reactor Data

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A batch reactor designed to simulate the non-isothermal temperature profile of a commercial, vertical-tube wet oxidation process is used to predict global process performance, and to estimate reaction rates. A model is developed for the batch reactor that predicts extent of reaction and vapor/liquid equilibria under non-isothermal conditions. This model is used with measured rate parameters to predict the effect of process conditions on overall performance of specific wastes. This reduces the number of runs normally executed in a feasibility study, saving time and money. Phenol is selected as a model compound, and values for reaction rate constants and induction period length are obtained for temperatures up to 224°C.

INTRODUCTION

Wet oxidation is the chemical reaction between molecular oxygen and dissolved or suspended organic material in liquid water, generally at temperatures above 175°C. The total pressure is kept above the vapor pressure of water to minimize boiling of the bulk liquid and improve the solubility of oxygen. The liquid serves as an excellent heat transfer medium to moderate the temperature increase resulting from exothermic oxidation reactions.

Wet oxidation was originally applied in the pulp and paper industry to oxidize waste lignin in black liquor into carbon dioxide and water [1, 2]. Since then it has been used during most of this century to successfully treat municipal sludge and other high strength wastes [3]. Wet oxidation processes are generally categorized according to the operating conditions relative to the critical point of pure water (374°C, 221 bar). A recent advance in the commercialization of sub-critical wet oxidation has been the development of a vertical-tube process.

The unique design of the vertical-tube process consists of small-diameter concentric tubes suspended below-ground to depths between 1200 and 1500 meters. The hydrostatic pressure created by the extreme depths eliminates the need for high-pressure surface pumps, and the high length-to-diameter ratio (~12000) provides ideal plug flow [4]. Additionally, the co-current flow of waste with pure oxygen provides good contact between the vapor and liquid. Development of this vertical reactor system began as part of a United States Environmental Protection Agency (USEPA) research study [5]. The system demonstrated effective oxidation of municipal wastewater solids while yielding a highly biodegradable effluent and usable solid residue. These results and favorable economics forecast by

the study led to the construction of the world's first commercial installation in the Netherlands [6].

The main reactor of the commercial, vertical system consists of two concentric pipes: the outer one sealed at the bottom. Waste, mixed with oxygen, is pumped into the center pipe and returns as process effluent up the annular space between the two pipes. Under steady-state operation, the exothermic oxidation reactions generate heat that is transferred between the countercurrent process flow and a surrounding cooling water jacket (Figure 1). Thus, heating and cooling the process stream accounts for a significant portion of a typical temperature profile.

Development of commercial projects require that the specific waste stream be evaluated for specific reaction rates and products of oxidation. These data are ultimately used to design a full-scale reactor system, and predict the quality of the process effluent. The traditional scale-up from laboratory experiments through pilot-plant trials to full-scale design is not a practical option in the case of the vertical reactor system. Achieving the temperature and pressure profiles of the full-scale reactor is difficult and expensive to do in an above-ground, flow-through unit with any meaningful capacity. Alternatively, a laboratory batch reactor can simulate the process history of a finite volume as it travels the length of the vertical reactor. Recalling that the

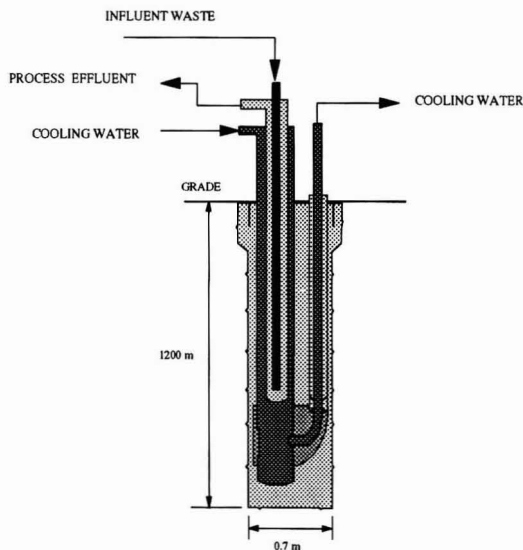


FIGURE 1 The vertical-tube, wet oxidation system.

full-scale process is a plug flow reactor, this arrangement is very effective as a simulation tool.

This paper describes the modeling and data analysis of a laboratory reactor designed to evaluate global process performance of the vertical wet oxidation process. The author's goal is to use this laboratory reactor system to evaluate kinetic parameters, and, in turn, apply these data to the reactor model to predict global process performance of a vertical-tube reactor. By modifying the operation of the laboratory unit kinetic constants were measured for a high-strength phenol solution and compared with published values. The applicability of these data with standard kinetic models were verified with the model.

THE BATCH REACTOR

The batch reactor is an insulated stainless steel cylinder (1.8 m length \times 5.1 cm ID) with a capacity of 2.7 liters mounted on a steel frame. To provide good mixing, an electric motor swings the reactor about its central diameter, analogous to a cylinder gently rocked back-and-forth, end-over-end. The sample (approximately one liter volume) is injected into the reactor using compressed air. The air is purged with pure oxygen which is added to the reactor in sufficient molar quantity to oxidize the total chemical oxygen demand (COD) of the sample. Electric heaters mounted on the reactor wall provide heat while cooling is accomplished by running water through jackets also mounted on the reactor wall. A filling reservoir, sample ports, temperature and pressure indicators, and appropriate valves and relief devices complete the unit (Figure 2).

Whereas a batch reactor simulating full-scale temperature profiles provides an accurate estimate of global process performance, an isothermal reactor is traditionally used to obtain more detailed kinetic information necessary for process optimization. Isothermal conditions are achieved by minimizing the heat-up and cool-down periods during operation. In continuous-flow reactors, rapid heat-up and cool-down is achieved with tubular reactors operating with small volumes. In stirred, batch reactors, concentrated sample is injected into a volume of dilution water pre-heated to the desired operating temperature. Whether continuous-flow or batch, these reactors typically maintain a continuous flow of oxidizing gas.

It is not practical with either of these traditional systems

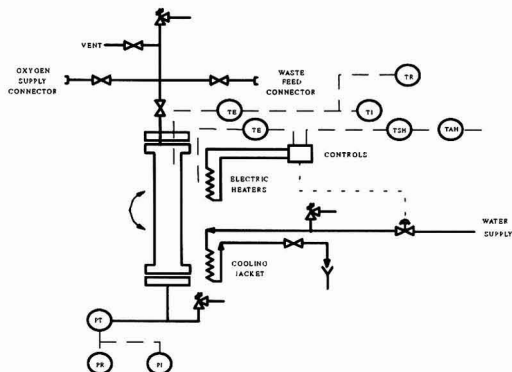


FIGURE 2 The batch reactor system.

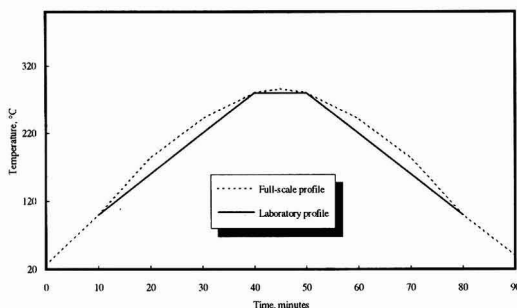


FIGURE 3 Comparison between pilot-scale and full-scale temperature profile.

to properly simulate the conditions of the vertical-tube reactor, and generate sample volumes sufficient for analysis. A tubular reactor can simulate the temperature profile, but is subject to scaling and cannot efficiently process significant volumes of sample, particularly municipal wastewater solids. A stirred, batch reactor operated with a finite vapor volume, as required for vertical-tube simulation, has high oxygen transfer resistance relative to the vertical-tube conditions. However, the physical construction of a laboratory system that overcomes these limitations precludes the rapid heat-up and isothermal sample injection required for traditional kinetic studies. Furthermore, the expenses associated with maintaining and operating two separate laboratory or pilot systems are usually prohibitive and unjustified relative to specific projects.

In the commercial system, the characteristic temperature profile results from the exchange of reaction heat between process flow and cooling water flow. As waste is pumped down the reactor it gradually heats up to a maximum (peak) downhole temperature that is sustained for a specific residence time, and cools as it makes its way back up the annular section. A programmable controller on the laboratory unit regulates the heater output and cooling water flow to reproduce this time/temperature profile. The resulting profile closely approximates the actual full-scale profile (Figure 3).

During typical operation, the reactor is sealed with the waste sample and the required mass of oxygen. The reactor is heated at a prescribed rate to the selected peak temperature where it is held for a predetermined residence time. Again, following a specific rate, the reactor is cooled to ambient conditions before the sample is withdrawn and tested. Kinetic information is obtained by sampling during the run, and measuring the extent of reaction as a function of time.

A feasibility study will often require a campaign of runs testing a specific sample at various peak temperatures and residence times. Understanding the effect of these process parameters is necessary for process optimization. However, a feasibility study test matrix may consist of twenty to thirty runs, an expensive undertaking particularly if testing occurs on location. One advantage of a detailed model of the laboratory reactor would be to generate the feasibility curves based on measured kinetic parameters. Fewer runs would be required to verify these curves and to obtain the kinetic data. This would translate as a significant savings in valuable laboratory time and resources.

EXPERIMENTAL METHODS AND PROCEDURE

Experimental Procedure

Availability of published kinetic data promoted phenol as a choice of the model compound for this study. The work of previous investigators served as a benchmark against which the results of this study could be compared. The high solubility and low volatility of phenol simplified some of the equilibrium calculations.

Using a traditional method, specific rate constants were determined from the slope of a semi-log plot of concentration versus time. Isothermal samples were obtained by heating the reactor and holding at a predetermined temperature, and withdrawing samples over a period of time. Since the initial sample is loaded under ambient conditions, some oxidation takes place during the heating period. However, a high initial organic concentration ensured that a negligible fraction of the total organic matter oxidized during this heat-up period. For purposes of data analysis, the initial concentration of organic species was defined as the concentration measured at the point that peak temperature was attained.

Activation energies were obtained from regression analysis between specific rate constants and temperature. The specific rate constants and the activation energy were calculated assuming excess oxygen. Therefore, the frequency factor is a lumped term of oxygen concentration and the rate constant.

Analytical and Computational Methods

Phenol solutions were prepared from solid reagent-grade phenol prior to each run. Initial concentrations were approximately 15 g/L. Samples for chemical oxygen demand (COD) analysis were digested using a dichromate reflux method and analyzed photometrically.

Execution of the mathematical reactor simulation was done using MathCad 5 Plus[®] software. The computational procedure for solving the differential equations uses a fourth-order Runge-Kutta method. Linear functions were estimated using a traditional least-squares regression method.

MODEL DEVELOPMENT

The reactor model predicts extent of reaction and vapor/liquid equilibria of the major gaseous components for a non-isothermal run. The model will verify the validity of kinetic data obtained by the methods described above. It accomplishes this by predicting the extent of oxidation based on experimentally obtained kinetic constants, and comparing the predicted profile with actual data.

Temperature Profile

The significant period of heat-up and cool-down during a reactor run (approximately 20 minutes each) requires accounting for kinetic behavior during this time. The use of a sophisticated controller allowed the heat-up and cool-down slopes to be accurately regulated to a constant slope. Thus, temperature in the reactor could be expressed as a function of time thereby reducing the model algorithm to one independent variable. A typical profile is illustrated in Figure 4.

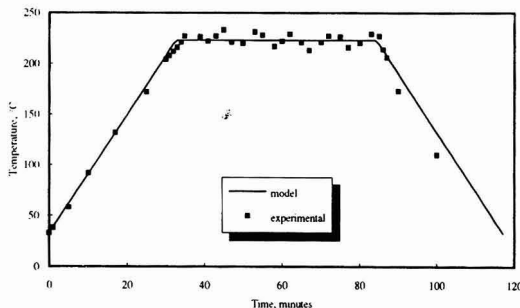
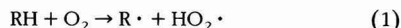


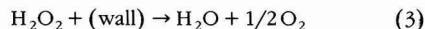
FIGURE 4 Typical temperature profile—actual and model prediction.

Kinetic Models

Wet oxidation of organic compounds is generally considered to proceed via free-radical mechanisms [7]. Free radicals are formed by the reaction of oxygen with the weakest C-H bonds of the target compound, R (Equations 1 and 2).



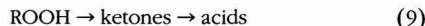
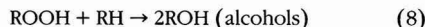
Hydrogen peroxide is the product of the second reaction (Eq. 2). However, it quickly decomposes on the surface of the reactor and other heterogeneous or homogeneous species to generate hydroxyl radicals (Equations 3 and 4) [8, 9].



The hydroxyl radical oxidizes the organic compound, RH, yielding the organic radical, R· (Equation 5). The organic radical in turn reacts with oxygen to produce the peroxy radical, ROO· (Equation 6). The peroxy radical abstracts a hydrogen from the organic compound to produce the unstable hydroperoxide (ROOH) and another organic radical (Equation 7). These reactions (Equations 1 through 7) represent the chain process by which radicals are formed.



The chain reactions terminate primarily from the reaction of the unstable hydroperoxide with organic compounds to yield alcohols or its decomposition to ketones and eventually acids (Equations 8 and 9).



The key step in this mechanism is attack by oxygen on the α -carbon, forming acetic acid as the major intermediate. Shibaeva *et al.* concluded that phenol oxidation proceeds via free radical formation [10].

Two distinct reaction periods usually characterize free-radical mechanisms: an induction period and a rapid oxidation period. The induction period, during which radicals are formed, is often the rate-limiting step. Slow oxidation can occur during this period. The model incorporates the induction period length estimate proposed by Willms *et al.* [11].

$$t_i = \frac{k_i}{\exp\left(\frac{-E_i}{RT}\right)[O_2]} \quad (10)$$

Thus, rapid oxidation will not occur before the required time, t_i , has elapsed. Of course, the length of the induction period is a function of temperature so that its magnitude depends on the temperature profile.

The most widely accepted global model for the oxidation of phenol is:

$$\frac{dCOD}{dt} = -k_o \exp\left(\frac{-E_a}{RT}\right)[COD]^a [O_2]^b \quad (11)$$

Consistent with previous studies the model will be assumed to be first-order in organic for both the induction-phase oxidation and the rapid oxidation. The oxygen charge is sufficient to satisfy more than all the COD requirement since the reactions are not carried to completion (see Equation 21). Therefore, the oxygen is in excess, and the reaction order with respect to oxygen reduces to zero. Equation 11 then yields the two series reactions:

$$\frac{dCOD}{dt} = -k_s \exp\left(\frac{-E_{a_s}}{RT}\right)[COD] \quad (12)$$

$$\frac{dCOD}{dt} = -k_f \exp\left(\frac{-E_{a_f}}{RT}\right)[COD] \quad (13)$$

Equations 12 and 13 can be rearranged to yield a differential equation in terms of organic conversion. This is particularly useful for simplifying the numerical evaluation of these equations, and precluding an organic concentration input for the simulation.

$$[COD] = [COD]_0(1 - X) \quad (14)$$

$$\frac{dX}{dt} = k(1 - X) \quad (15)$$

The above equations are combined to yield the overall oxidation kinetics upon which the model algorithm is based (Equation 16).

$$\frac{dX}{dt} = k \exp\left(\frac{-E}{RT}\right)(1 - X) \left\{ \begin{array}{l} k = k_s \quad t \leq t_i \\ k = k_f \quad t > t_i \end{array} \right\} \quad (16)$$

Vapor/Liquid Equilibrium

Equilibrium calculations in the model apply Henry's Law to estimate partitioning of oxygen, carbon dioxide, and water between vapor and liquid phases. Harvey and Sengers propose a correlation between the partial pressure of water and temperature to estimate the Henry's constant for oxygen in water [12].

$$T \ln\left(\frac{H_{O_2}}{P_w}\right) = 1319.6 + 4.517(p_w - 322) - 8.229 \times 10^{-4} T p_w e^{273.15 - T/50} \quad (17)$$

The water vapor pressure is given by the Antoine Equation.

$$\ln P_w = 65.1544 - \frac{6842.91}{T} + 2.78351 \times 10^{-3} T - 6.13638 \ln(T) + 3.31168 \times 10^{-18} T^6 \quad (18)$$

The Henry's Law constant for carbon dioxide was regressed to a general formula using solubility data at 100 bar.

$$\ln H_{CO_2} = -97.4394 + \frac{1220.93}{T} + 22.3906 \ln T - 0.04852775 T \quad (19)$$

In each of the above correlations the variables are expressed in the following units: the Henry's constant in N/m²; temperature in K; and density, ρ , in kg/m³.

Further vapor/liquid equilibrium considerations must be given in the case of volatile organic species. Willms *et al.* have developed a detailed model for analyzing kinetic data that accounts for the repartitioning of the volatile species between vapor and liquid [13]. The model corrects observed kinetic rate by a factor that is a function of the Henry's constant for the organic species.

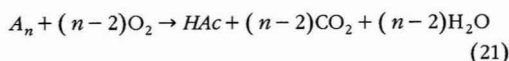
$$\phi = \frac{V^l}{V^l + \frac{H_{organic} MW_w}{RT \rho_w} (V^l - V^l)} \quad (20)$$

Phenol is infinitely soluble in water under the conditions of this study, and has a relatively low vapor pressure. Thus, its respective Henry's constant is assumed to be zero, and the correction factor reduces to one.

Oxygen and Carbon Dioxide Mass Balances

The total molar quantity of oxygen and carbon dioxide at any time depends on the extent of reaction. An organic component can be characterized by its equivalent oxygen demand, and, in complete combustion, this oxygen demand is equal to its total chemical oxygen demand (COD). In sub-critical wet oxidation, the oxidation does not go to completion. Rather, acetic acid forms as a result of scission reactions and its relatively high activation energy makes it resistant to further oxidation under sub-critical conditions with several investigators reporting it as a major wet oxidation by-product [14, 15, 16].

Li *et al.* have proposed a global reaction equation that accounts for the formation of acetic acid [17]. For an organic compound having n number of carbon atoms the stoichiometric oxygen requirement is given by



Therefore, the oxygen demand for wet oxidation of compound A in sub-critical wet oxidation reactions is equal

to a fraction of its theoretical oxygen demand (COD). Thus, the oxygen consumption can be estimated by multiplying the theoretical oxygen demand by an oxygen demand correction factor, f_{COD} (Equation 22). The correction factor for phenol is 0.57.

$$f_{COD} = \frac{(n-2) \times 32}{MW_{organic}} \times \left(\frac{1}{COD} \right) \quad (22)$$

Based on this discussion, the total molar quantity of oxygen at any time can be expressed in terms of the initial concentrations of oxygen and the chemical oxygen demand of the organic compound.

$$n_{O_2}^t = \frac{n_{O_2,0}^i MW_{O_2} + V^l (f_{COD})(COD_0 - COD)}{MW_{O_2}} \quad (23)$$

The concentration of oxygen required for Equation 10 arises from partitioning the initial oxygen mass between the liquid and vapor phase. Assuming that the liquid mole fraction of water is much greater than that of oxygen or carbon dioxide, it follows that the molar quantity of liquid mass is approximately equal to the moles of water in the liquid phase. Applying Henry's Law and the foregoing assumption, the molar quantity of oxygen in the vapor phase becomes

$$n_{O_2}^v = \frac{n_{O_2}^t}{\frac{n_w^i RT}{V^v H_{O_2}} - \frac{P_w}{H_{O_2}} + 1} \quad (24)$$

Implicit in this analysis is the assumption that mass transfer between vapor and liquid is extremely fast relative to the reaction rate. This assumption precludes use of an oxygen mass transfer term in calculating vapor/liquid equilibria, and simplifies Equation 24. Given the agitative motion of the reactor, one can intuitively expect good mass transfer in this type of system. Verification of this assumption is discussed in a later section.

From Equation 21, the total molar quantity of carbon dioxide is equal to the amount of oxygen consumed in the oxidation reaction. Thus,

$$n_{CO_2}^t = n_{O_2,0}^i - n_{O_2}^t \quad (25)$$

A treatment similar to Equation 24 can then be applied to calculate the concentration of carbon dioxide in the vapor.

$$n_{CO_2}^v = \frac{n_{CO_2}^t}{\frac{n_w^i RT}{V^v H_{CO_2}} - \frac{P_w}{H_{CO_2}} + 1} \quad (26)$$

Partial Pressures and Total Pressure

The calculated molar vapor concentrations of oxygen and carbon dioxide easily lead to their respective vapor pressures. Assuming ideality, the partial pressure of oxygen and carbon dioxide are estimated as

$$P_{O_2} = \frac{n_{O_2}^v RT}{V^v} \quad (27)$$

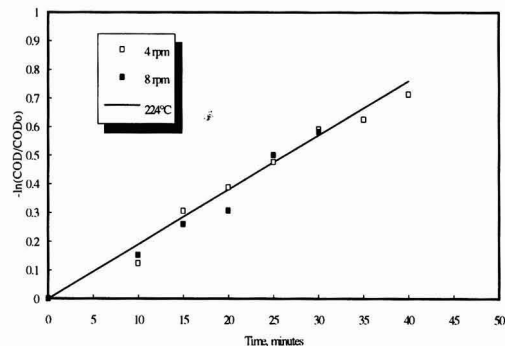


FIGURE 5 Effect of reactor rocking frequency on phenol oxidation rate.

$$P_{CO_2} = \frac{n_{CO_2}^v RT}{V^v} \quad (28)$$

The total pressure in the reactor at any time is the sum of the partial pressures (Equations 18, 27, and 28)

$$P_{total} = P_{CO_2} + P_{O_2} + P_{H_2O} \quad (29)$$

RESULTS AND DISCUSSION

Oxygen Transfer

Analysis of data from this system assumes rapid mass transfer of oxygen between the vapor and liquid phase. The only controllable parameter governing mass transfer is the reactor rocking frequency. To understand the effect of rocking frequency on oxygen transfer, two runs were executed at different rocking frequencies, all other conditions being identical.

The observed oxidation rate did not change when the rocking frequency doubled (Figure 5). Thus, mass transfer is independent of variations in the reactor hydrodynamics. This suggests that the prevailing hydrodynamic condition of this type mixing favors low resistance to oxygen mass transfer.

Kinetic Constants

As expected, the oxidation of phenol proceeds slowly during the induction period. As the reaction progresses with time, an initial period of rapid COD reduction takes place (Figure 6). Specific rate constants are calculated from each of these oxidation periods. These rate constants are evaluated by integrating Equations 12 and 13 to yield a linear relationship between organic reduction and time. In the case of rapid oxidation, the reaction is assumed to be zero-order with respect to oxygen. The specific rate constant is calculated directly from the slope of each line.

Assuming an Arrhenius relationship between these rates, activation energies are calculated for the two oxidation periods (Figure 7). The activation energy for the induction period oxidation is 160.76 kJ/mol. There is no literature value reported in this temperature range to compare against. For rapid oxidation, the activation energy is

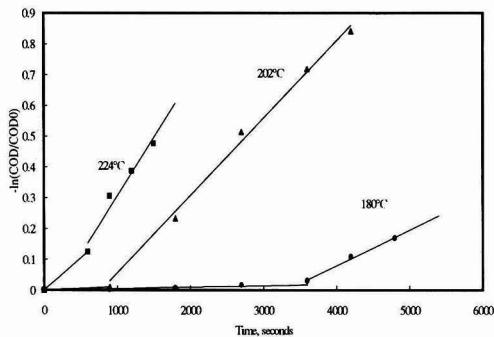


FIGURE 6 The oxidation of phenol; induction period and rapid oxidation.

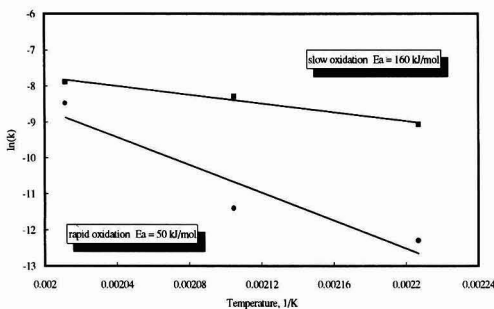


FIGURE 7 Phenol oxidation activation energies.

50.6 kJ/mol. This is consistent with values reported by Pruden and Le (45 kJ/mol) [18], and Joglekar *et al.* (48 kJ/mol) [19].

To complete the required constants for Equations 12 and 13, the pre-exponential factors, k_s and k_f , are required. From the Arrhenius equation we know that the specific rate constant is equal to the pre-exponential factor multiplied by the activation energy exponential factor. Applying this equation to the observed specific rate constants, the pre-exponential factors for the pseudo first-order slow and fast oxidation reactions are found to be 83.9 sec^{-1} and $1.1 \times 10^{13} \text{ sec}^{-1}$, respectively.

To calculate the constant for induction-phase length, Equation 10 is rearranged to yield a linear expression.

$$\ln(t_i [O_2]) = \ln(k_i) + \frac{E_i}{RT} \quad (30)$$

The quantity $(t_i [O_2])$ is obtained by estimating the length of the slow oxidation period during the isothermal steady-state operation, and multiplying it by the liquid oxygen concentration at that temperature. The oxygen concentra-

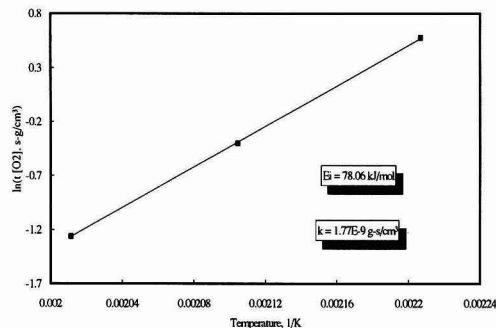


FIGURE 8 Induction phase analysis for phenol.

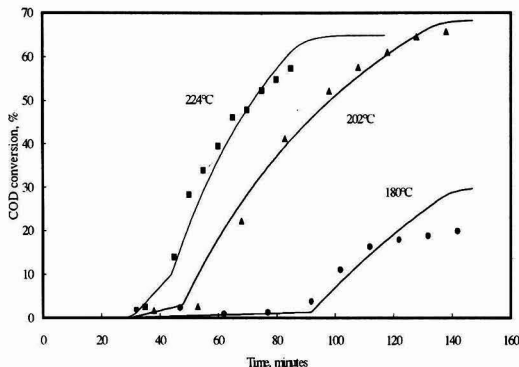


FIGURE 9 Comparison between predicted and actual phenol oxidation.

tion is estimated from vapor/liquid equilibrium calculations. Plotting this product against the reciprocal temperature yields a regression line with a slope of E_i/R and an intercept of $\ln(k_i)$ (Figure 8).

The preceding analysis ignores induction-phase length during the heat-up period. Since the induction-phase length is a function of oxygen concentration, it is variable during the heat-up period, and cannot be estimated from observation. However, at the lower temperatures the oxygen concentration is low, and for all three cases, the induction time during heat-up will be equally large relative to the observed time during steady-state operation. The analysis relies on the observable differences in induction-phase length which occur at steady-state temperatures.

Model Runs

Applying experimentally determined kinetic constants (Table 2) to the reactor simulation model yields predictions comparable to actual results (Figure 9). Near the end of the

TABLE 1. Specific reaction rates for the slow and rapid oxidation of phenol

	180°C	202°C	224°C
Specific reaction rate (slow oxidation), sec^{-1}	4.58×10^{-6}	1.10×10^{-5}	2.07×10^{-4}
Specific reaction rate (rapid oxidation), sec^{-1}	1.16×10^{-4}	2.52×10^{-4}	3.79×10^{-4}

TABLE 2. Summary of first-order kinetic constants for phenol oxidation

	Activation energy, kJ/mol	Rate constant, $g \cdot s/cm^3$ or 1/sec
Induction-phase length	78.06	1.77×10^{-9}
Induction-phase oxidation	160.76	1.09×10^{13}
Rapid oxidation	50.65	8.39×10^1

rapid oxidation period, the model predicts higher conversions than the actual results indicate. This is especially evident in the lower temperature run. This behavior has been observed by others [20], and Willms *et al.* have proposed that this is caused by a buildup of partially oxidized intermediates that compete with the parent organic for free radicals [17].

The liquid-phase oxygen concentration predicted by the model is useful in understanding the availability of oxygen during the reactions. As illustrated in Figure 10, the maximum oxygen liquid-phase concentration occurs at the instant peak temperature is reached. As COD is oxidized the available oxygen steadily decreases as carbon dioxide levels increase. The nearly linear uptake suggests that the assumption of oxygen excess is valid.

CONCLUSIONS

Kinetic data obtained using the reactor described in this study is accurate, and comparable to literature values obtained by more conventional reactor systems. Although the material tested undergoes a significant period of heating before rate constants are measured, the final evaluation is not affected. The reason is probably twofold. First, wet oxidation reactions generally do not progress below temperatures of 175°C. Secondly, operating with samples with relatively high COD concentrations allows that any oxidation that does take place during the heat-up period is but a small fraction of the total oxidation effected during the isothermal portion of the run. In this way, kinetics can be evaluated under isothermal conditions by defining the initial concentration as the concentration at the time peak temperature is reached.

The simulation model for the laboratory batch reactor effectively predicts extent of reaction and vapor/liquid equilibrium. By adjusting the inputs that describe reactor condi-

tions the model can be used to predict performance under different conditions of temperature and residence times. Since the residence time at peak temperature does not usually exceed 10–15 minutes for a full-scale process run, the limitation of the model at higher conversion rates is not an issue. Thus, it is possible to generate feasibility curves for a specific waste once kinetic parameters are evaluated. This way numerous laboratory experiments can be eliminated that were previously required to generate these curves.

NOTATION

- A = organic compound
- [COD] = chemical oxygen demand liquid concentration
- E = activation energy
- f = defined in Equation 22
- H = Henry's constant
- HAc = acetic acid
- k = reaction rate constant
- MW = molecular weight
- n = number of moles
- [O₂] = liquid oxygen concentration
- P = pressure
- R = universal gas constant
- t = time
- T = temperature
- V = volume
- X = organic conversion

Greek symbols

- α = order with respect to organic
- β = order with respect to oxygen
- φ = defined in Equation 20
- ρ = density

Subscripts

- 0 = initial
- COD = chemical oxygen demand
- CO₂ = carbon dioxide
- f = rapid oxidation
- i = induction phase
- n = number of carbon atoms
- o = global reaction
- O₂ = oxygen
- s = induction-phase oxidation
- w = water

Superscripts

- l = liquid
- t = total
- v = vapor

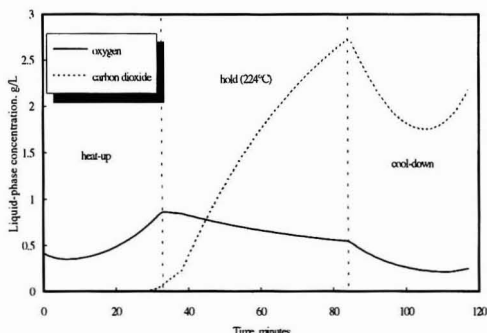


FIGURE 10 Liquid-phase concentration profile for oxygen and carbon dioxide (224°C).

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LITERATURE CITED

1. **Strehlenert, R. W.**, U.S. Patent No. 1,149,420 (Aug. 1915).
2. **Metcalf and Eddy, Inc.**, *Wastewater Engineering: Collection, Treatment, and Disposal*, McGraw-Hill Book Company, New York, pp. 368–369 (1972).
3. **Teletzke, G. H.**, "Wet Air Oxidation," *Chemical Engineering Progress*, **60**(1), pp. 33–38 (Jan. 1964).
4. **Rappe, G. C.**, "New Sludge Destruction Process," *Environmental Progress*, **4**(1), pp. 56–60 (Feb. 1985).
5. **City of Longmont, Colorado**, "Aqueous-Phase Oxidation of Sludge Using the Vertical Reaction Vessel System," US EPA Report No. CS-809337-01 (Mar. 1987).
6. **Bowers, D. L., et al.**, "The VerTech Aqueous-Phase Oxidation Process," *Water, Environment, and Technology*, **3**(11), pp. 64–68 (Nov. 1991).
7. **Emanuel, N. M., et al.**, *The Oxidation of Hydrocarbons in the Liquid Phase*, Pergamon Press, New York, pp. 1–3 (1965).
8. **Emanuel, N. M., et al.**, *Liquid-Phase Oxidation of Hydrocarbons*, Plenum Press, New York, p. 153 (1967).
9. **Schumb, W. C., et al.**, *Hydrogen Peroxide*, Reinhold Publishing, New York, pp. 523–525 (1955).
10. **Shibaeva, L. V., et al.**, "Oxidation of Phenol with Molecular Oxygen in Aqueous Solutions," *Kinetic Catalysis*, **10**(5), pp. 832–836 (Sept. 1969).
11. **Willms, R. S., et al.**, "Aqueous-Phase Oxidation: The Intrinsic Kinetics of Single Organic Compounds," *Ind. Eng. Chem. Res.*, **26**(1), pp. 148–154 (1987).
12. **Harvey, A. H., and J. M. H. L. Sengers**, "Correlation of Aqueous Henry's Constants from 0°C to the Critical Point," *AIChE J.*, **36**(5), pp. 539–536 (Apr. 1990).
13. **Willms, R. S., et al.**, "Analysis of High-Pressure, Multiphase, Batch Reactor Data," *Environmental Progress*, **4**(2), pp. 131–135 (May 1985).
14. **Skaates, J. M., et al.**, "Wet Oxidation of Glucose," *The Canadian Journal of Chemical Engineering*, **59**, pp. 517–521 (Aug. 1981).
15. **Bailod, R. C., et al.**, "Fate of Specific Pollutants During Wet Oxidation and Ozonation," *Environmental Progress*, **1**(3), pp. 217–227 (Aug. 1982).
16. **Foussard, J., et al.**, "Efficient Elimination of Organic Liquid Wastes: Wet Air Oxidation," *Journal of Environmental Engineering*, **115**(2), pp. 367–385 (Apr. 1989).
17. **Li, L., et al.**, "Generalized Kinetic Model for Wet Oxidation of Organic Compounds," *AIChE J.*, **37**(11), pp. 1687–1697 (Nov. 1991).
18. **Pruden, B. B., and H. Le.**, "WAO of Soluble Components in Waste Water," *Can. Journ. of Chem. Eng.*, **54**, pp. 319–325 (Aug. 1976).
19. **Joglekar, H. S., et al.**, "Kinetics of WAO of Phenol and Substituted Phenols," *Water Research*, **25**(2), pp. 135–145 (1991).
20. **Chowdhury, A. K., and L. W. Ross**, "Catalytic Wet Oxidation of Strong Waste in Waters," *AIChE Symposium Series No. 151*, **71**, p. 46 (1975).

Waste Minimization by Process Modification

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The goal of this research is to show that source reduction through process modification is a viable technique to minimize process waste. To accomplish this objective, the allyl chloride process was studied. The approach involved three steps: process modeling, selection of source reduction variables and their ranges, and optimization of an economic objective function. The simulator ASPEN PLUS™ was used to model and evaluate the process. Source reduction variables were primarily located through the literature as well as a sensitivity analysis. To find the best value of these process variables, optimization of an economic objective function was performed. The general methodology developed through this work gave structure to this research and was found to be a useful approach in determining economical waste minimization optics.

INTRODUCTION

Society's increasing environmental awareness has forced the government to pass more stringent environmental laws. These laws have put both economical and societal pressure on companies to clean up chemical processes. Such current and anticipated future regulations regarding environmental pollution have created the need to significantly change the manufacturing philosophy in this country. The major impact of these regulations is the requirement that companies must re-analyze their current schemes for chemical waste reduction and develop new strategies for minimizing the production of waste and hazardous chemicals.

There are many benefits in developing new strategies for waste minimization. As a member of society, one wants to leave a clean environment for the generations that will follow. In addition, a more efficient process with less waste is an economic incentive. For a company, there are also intangible benefits: improved corporate image and reduced environmental liability. Regardless of the reason, companies are changing the way they view pollution.

This research is designed to develop a strategy for reducing waste by the source reduction technique of process modification. Examples of process modifications can be adjustment of reactor conditions and types, feed ratios, and general operating parameters. Although process modifications might entail capital costs, they will provide an environmental cost saving by reducing waste treatment costs.

In addition, less waste means a more efficient process and a reduction in the risk to human health and the environment.

BACKGROUND

The promulgation of the Pollution Prevention Act (PPA) of 1990 exhibits the trend of American governmental policy. Although this legislation is not enforceable, it symbolizes the attitude of society and their views on the preservation of the environment. The PPA indicates the importance of preventing pollution, whether through waste treatment, source reduction, or recycling.

In the past ten years many companies have actively pursued pollution prevention programs. However, despite extensive interest in the concept of waste minimization, pollution prevention initiatives are rare in most companies [1]. Even though pollution prevention seems to work companies are still not buying into the concept. Corporate management holds the same resistance to waste reduction as was formally put up against total quality management. Similarly, it needs to be thought of as just "a good way to do business" [2].

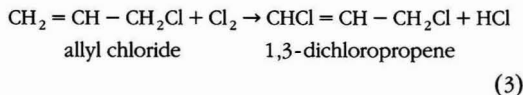
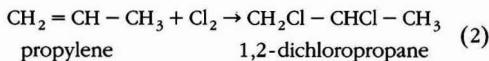
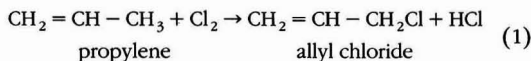
Reduction of waste at the source is one such strategy that is replacing the more traditional method of end-of-pipe waste treatment. The Environmental Protection Agency (EPA) prefers source reduction over waste treatment for waste minimization because it eliminates the waste before it occurs. Source reduction reflects a new long-term philosophy that advocates anticipation of a problem (waste) before it happens (is generated). Many companies find this strategy difficult since it means incurring a capital cost which may be larger than a current annual cost for waste treatment. Thus this work shows how such new waste minimization strategies, like source reduction, can be implemented cost effectively. The objective of this work is to develop a source reduction methodology by applying source reduction techniques to the allyl chloride (3-chloropropene) process.

Currently, the waste limits imposed on companies for processes are technology based standards. In other words, the technology used in a process must perform so that process effluents do not exceed designated waste levels. However, in the future the EPA will emphasize risk based regulations of waste. Most companies are knowledgeable on technology based standards but lack expertise on the application of regulatory risk to process design or debottlenecking. To account for these inadequacies, this work shows how regulatory risk analysis could be incorporated as an economical optimization constraint.

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The allyl chloride process is an ideal vehicle for applying process modification. Allyl chloride is a colorless, mobile liquid that is only slightly soluble in water [3]. The allyl chloride process provides an opportunity for reducing the effluents of several toxic pollutants regulated by the EPA. The product, allyl chloride, has been labeled as a very volatile hazardous air pollutant (vvhap) [4]. Two of the primary by-products, 1,2-dichloropropane (12DCP) and 1,3-dichloropropene (13DCP) are less hazardous and therefore listed under the title of volatile organic hazardous air pollutants (vohap) [4]. Both of these by-products are also on the Clean Water Act's list of priority pollutants [5]. In addition, all three chemicals are regulated under the recent Hazardous Organic National Emission Standards for Hazardous Air Pollutants (Hazardous Organic NESHAPs or HON) [6] implemented by the Clean Air Act.

Allyl chloride is usually produced from high temperature (300–600°C) chlorination of propylene (propene). Although many by-products are formed in this reactor, the primary by-products are 12DCP and 13DCP.



The reaction products leaving the reactor are cooled and fed to a prefractionator, where the overhead products are primarily hydrogen chloride and unreacted propylene and the bottom products are chlorinated hydrocarbons. The hydrogen chloride is removed from the distillate product via absorption with water, forming commercial grade aqueous hydrogen chloride. The propylene is then washed with caustic soda to remove the hydrogen chloride. After compression and condensation to remove water the propylene is recycled to the reactor. Three distillation columns are used to separate the bottoms product of the prefractionator into allyl chloride and the dichloride by-products. The process modification techniques were developed to reduce the waste by-products, 12DCP and 13DCP.

GENERAL APPROACH

This research follows a three step approach. First, the process was modeled on the simulator, ASPEN PLUS™. The process variables, including the kinetic data and approximate temperatures and pressures were obtained from the literature [7, 8] and yielded a process model that produced good results.

The next phase was the determination of source reduction variables (SRVs). For example, if modifying the reactor temperature directs the reaction selectivity away from by-product formation, then the reaction temperature is a SRV. The SRVs and their ranges were determined through sensitivity analysis and published information [3, 9].

In the final stage, the waste reduction options were found by implementing the SRVs into the simulated process. However, because some SRVs were non-continuous and

could not be varied in a single simulation, four optimizations were performed. Since altering the SRVs affected other parameters besides the by-product formation, the model was optimized economically. Economic optimization allowed for the evaluation of the impact of several SRVs on utility and raw material costs. The environmental costs were incorporated through waste treatment costs. Through the use of this preliminary economic model, waste reduction is no longer based on the least possible waste. It is instead based on the least possible economically feasible waste.

Economics and Optimization

Although the SRVs could be optimized to find a waste reduction option (WRO) that outputs the lowest waste, this operating scheme might not always be economical. For instance, an WRO might reduce the waste, but require that the company operate with a negative cash flow. Since this is clearly unacceptable, economics must be linked with the objective function that optimizes the simulation.

An objective function in terms of preliminary profit was developed which incorporates both the revenues and costs of the process.

$$\text{Preliminary Profit} = \frac{\text{Product Revenue}}{\text{Revenue}} - \frac{\text{Raw Material Cost}}{\text{Cost}} - \frac{\text{Utility Cost}}{\text{Cost}} - \frac{\text{Waste Treatment Cost}}{\text{Cost}} \quad (4)$$

The revenues and costs in Equation (4) can be further broken down as follows:

$$\text{Product Revenue} = \text{Allyl Chloride} + \text{HCl} \quad (5)$$

$$\text{Raw Material Cost} = \text{Propylene} + \text{Chlorine} \quad (6)$$

$$\text{Utility Cost} = \text{Fuel} + \text{Electricity} + \text{Cooling Water} \quad (7)$$

$$\text{Waste Treatment Cost} = 12\text{DCP} + 13\text{DCP} + \text{Unused Chlorine} \quad (8)$$

The fixed costs that any economic analysis will have such as labor, maintenance, etc. were not included in the objective function since they will not be significantly changed by the process modifications.

For each of the four cases analyzed, ASPEN PLUS™ was used to find the maximum value (maximum profit) of the objective function. In other words, the simulator's optimization routine changes the SRVs to find the optimal value the SRVs that yields the highest profit.

PROCESS MODEL

Process Characterization

In the first phase of modeling, a skeleton of the process diagram with a plug flow reactor (PFR) was developed on ModelManager™. First the feed streams, heaters/coolers, reactor, and separation equipment were modeled. The propylene feed was determined by back-calculation from actual estimated production values [3]. The heaters and coolers were modeled as HEATER blocks, which only required outlet temperature specifications.

Initially, the reactor was specified as a PFR (RPLUG-block) in order to validate the kinetic data provided by

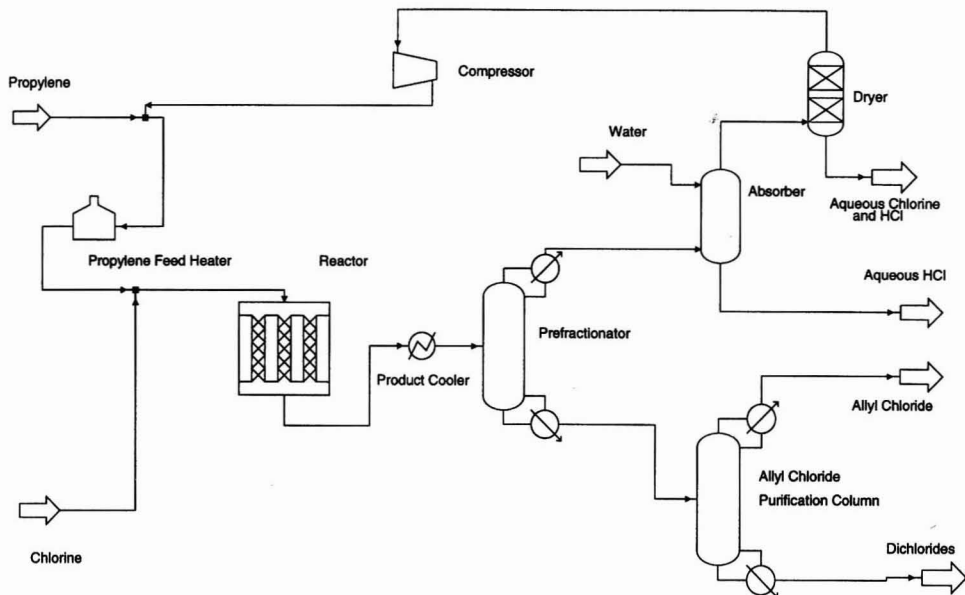


FIGURE 1 ASPEN PLUS™ flowsheet of the allyl chloride process.

Biegler and Hughes [7]. The activation energy and pre-exponential factor were based on partial pressure concentrations. However, ASPEN PLUS™ requires that these kinetic data be in terms of mass concentration. Thus, the kinetic data were re-plotted in terms of mass concentration and a new activation energy and pre-exponential factor were determined [10].

To avoid problems and to make the simulation easy to debug, shortcut distillation blocks (DSTWU) were used for the distillation columns. The DSTWU block uses Winn's method to estimate the minimum number of stages, Underwood's method to estimate the minimum reflux ratio, and Gilliland's correlation to estimate the required reflux ratio for specified number of stages or the required number of stages for a specified reflux ratio.

Once all the errors had been removed from the initial simulation, more units were added to complete the simulation. The results from the shortcut distillation blocks, number of stages and reflux ratio, were used in a more rigorous distillation model (RADFRAC). When first implemented the RADFRAC blocks did not converge. This problem was alleviated by altering the reflux ratio and distillate vapor fraction. The process flow diagram for the complete simulation is shown in Figure 1 and unit operations and their corresponding ASPEN PLUS™ models are shown in Table 1.

When process modifications are performed on the process model they will cause changes in the composition and flow through the distillation columns. To ensure that the columns operated correctly, SPEC statements within the RADFRAC blocks were used to vary the distillate/feed ratio to give 99% product recovery in the prefractionator and 99.5% in the allyl chloride purification column.

The second phase of modeling also included the incorporation of the compressor and recycle portion of the process. For the recycle section, a DESIGN-SPEC block was used to vary the propylene feed based on the amount of

recycled propylene. This addition to the model kept the feed to the reactor constant.

Since it was necessary to evaluate a CSTR (see Table 2), a new input file was created. It had the identical process units as the PFR simulation with the exception of the RCSTR block used to model the CSTR. In addition, the DESIGN-SPEC used to keep the residence time constant had to be slightly altered to accommodate the available access variables for the RCSTR block.

SOURCE REDUCTION VARIABLES AND THEIR RANGES

Several sources were found in the literature [3], [9] that provided an abundance of information describing which variables had what effect on the process. Table 2 lists the source reduction variables used in this work.

The two variables that had the most effect on the amount of by-product formed are the reactor feed temperature and propylene chlorine feed ratio. Reactor pressure was added

TABLE 1 Unit Operations and Their ASPEN PLUS™ Models

Unit Operation	ASPEN PLUS™ Model
Reactors—plug flow reactor	RPLUG
cont. stirred tank reactor	RCSTR
Prefractionator	RADFRAC
Allyl Chloride Purification Column	RADFRAC
Absorber	RADFRAC
Propylene Feed Preheater	HEATER
Product Cooler	HEATER
Dryer	SEP
Compressor	COMP

TABLE 2 Source Reduction Variables and Ranges

Source Reduction Options	Range
Propylene/chlorine feed ratio	1 to 12
Reactor feed temperature	200 to 425 °C
Reactor pressure	170 to 350 kPa
Reactor classification	PFR and CSTR
Reactor operation	Adiabatic and Isothermal

to the list of source reduction variables even though in previous studies reactor pressure had not significantly affected the by-product formation.

SRV's Ranges

For each SRV, a range was determined from the sensitivity study. If the calculations showed potential for waste reduction outside this range, then the range was extended. The ranges for each SRV are shown in Table 2. From this range of variables an "experimental" grid was developed to explore the waste reduction potential of several of the variables.

A grid was developed that varied the feed ratio, feed temperature, and reactor pressure for each reactor classification and operation. Thus there were four grids evaluated: adiabatic PFR, isothermal PFR, adiabatic CSTR, and isothermal CSTR.

The ranges for each of the four grids varied according to the results of the sensitivity studies. For some grids a reactor pressure of 170 kPa caused calculation errors and for others it would not. Despite these differences the ranges did not extend outside those listed in Table 2.

OPTIMIZATION AND ECONOMICS

For each of the four cases (adiabatic PFR, isothermal PFR, adiabatic CSTR, and isothermal CSTR) the propylene feed

temperature, feed ratio, and reactor pressure were varied. The optimal values (those that yield the highest preliminary profit) for each case are listed in Table 3. Each case was evaluated based on a constant reactor residence time of 4 seconds.

The largest value of preliminary profit is obtained by operating the reactor as an isothermal plug flow reactor. For this case more reactant was used to produce more product than the other three cases, thus it had a higher revenue and higher costs. However, due to the high value of allyl chloride, the increase in revenue outweighed the increase in waste costs.

Although these results (higher yield for isothermal PFR) agree with the literature [3], [9], industrial reactors are usually adiabatic plug flow reactors. The amount of cooling required to operate isothermally is often difficult to achieve due to the high reaction velocity.

Optimal operation of both the adiabatic and isothermal continuous stirred tank reactors supplied a significantly lower preliminary profit. This lower profit was mainly due to lower product yield. In order for the CSTR to operate at the same economic level as the PFR, the CSTR's residence time must be increased. A longer residence time means a larger reactor and an increased cost, which would offset the increase in profit caused by higher product yield.

The utilities costs for each of the four cases did not have much effect on the preliminary profit. They remained fairly constant based on the reactor type. The plug flow reactors had utilities costs around \$250/hr, whereas the continuous stirred tank reactors had utilities costs of around \$380/hr. In a more rigorous economic approach, the utility costs would have a greater effect on the profit since the overhead costs, labor, maintenance, etc. would lower the profit.

Reactor Pressure

Optimal reactor pressures differed based on reactor type. Both CSTRs produced the highest profit at 345 kPa. In contrast, the optimal pressure for the PFRs were less than 345

TABLE 3 Economic Optimization Results

Variable	Adiabatic PFR	Isothermal PFR	Adiabatic CSTR	Isothermal CSTR
Source Reduction Variables				
Propylene Feed Temp. (°C)	376	420	309	260
React. Feed Ratio (C ₃ H ₆ /Cl ₂)	7.5	4.1	8.3	8.7
Reactor Pressure (kPa)	274	318	345	345
Products				
Allyl chloride (kmol/hr)	30.9	51.8	24.1	26.0
Aq. HCl (kmol/hr)	274	477	246	259
12DCP (kmol/hr)	8.50	19.9	6.93	7.30
13DCP (kmol/hr)	10.3	18.6	10.4	11.3
Unused chlorine (kmol/hr)	0.00	0.00	2.77 × 10 ⁻³	2.79 × 10 ⁻³
Economics				
Revenue (\$/hr)	6014	10200	5091	5258
Waste material costs (\$/hr)	1522	3135	1407	1504
Raw material costs (\$/hr)	1857	3394	1655	1739
Utilities costs (\$/hr)	239	255	379	384
Preliminary Profit (\$/hr)	2396	3418	1649	1631

TABLE 4 Reactor Temperature

Reactor Temperature	Adiabatic PFR	Isothermal PFR	Adiabatic CSTR	Isothermal CSTR
Inlet (°C)	361	392	298	249
Outlet (°C)	493	392	422	422
Avg./Oper. (°C)	427	392	422	422

kPa, varying from 274 kPa for the adiabatic case to 318 kPa for the isothermal case. Sensitivity analysis showed that the pressure had little effect on the yield or distribution of the products. Normally, this pressure is set by the pressure drop of the propylene circulation system of the plant.

Reactant Feed Ratio

For each case the propylene feed was kept constant at 453.6 kmol/hr while the chlorine was allowed to vary between 37.8 and 453.6 kmol/hr (feed ratio 12 to 1). Table 3 shows that the reactant feed ratio of propylene to chlorine varied from 4 to almost 9. As one would expect, there exists a direct correlation between the feed ratio and the product formation. As the feed ratio decreases (more chlorine is reacted), more products and by-products are formed.

Reactor Temperature

With the exception of the isothermal PFR, the reactors have similar average/operating temperatures (see Table 4). The maximum reactor temperature for the adiabatic PFR was close to the temperature suggested for industrial reactors [9].

Therefore, if allyl chloride was being produced with an adiabatic plug flow reactor, the economically optimal waste minimization strategy would be to adjust the propylene feed temperature to the reactor to 361°C to achieve a maximum outlet or ultimate temperature of 493°C reactor.

Regulatory Risk Analysis

In the future, risk based regulations will likely replace the current technology based standards. Thus, it is imperative that any waste minimization strategy involve regulatory risk analysis. Since information concerning location of the plant and its potential damage to its environment is not available, a complete quantitative risk analysis could not be performed. However, the methodology was developed and applied to show how risk analysis can be incorporated into process modification based waste minimization strategy to determine a maximum waste production level.

Usually the goal of risk assessment is to determine the risk of a leak or spill on the environment surrounding the plant. It follows four stage process created by the U.S. Academy of Sciences that includes: hazard identification, exposure assessment, toxicity assessment, and risk characterization [11]. In contrast, the intent for incorporating risk into a process modification based waste minimization strategy is to determine a maximum production level that will not pose a risk to the plant's environment. This maximum production level of a by-product can then be used as a constraint in the optimization routine.

The methodology developed for this research uses a six step approach that is broken into a qualitative section and a quantitative section as follows:

Qualitative:

1. Hazard identification—which chemicals are important,
2. Exposure assessment—where do the chemicals go, who might be exposed, and how,
3. Toxicity assessment—determining numerical indices of toxicity for computing risk,

Quantitative:

4. Risk level determination—maximum acceptable risk,
5. Maximum concentration evaluation—calculate the delivered concentration that causes the risk,
6. Exposure assessment—calculate what original concentration caused the delivered concentration.

In the first section, the traditional risk assessment steps are qualitatively followed in the designated order. Next, the methodology quantitatively follows these same steps in reverse order to back-calculate the maximum allowable waste level. It seeks to determine what quantity of waste produces the minimum acceptable risk as opposed to a risk assessment which calculates the risk caused by a certain amount of waste.

Although the preceding description is fairly simple, risk analysis is usually a complicated process involving several iterations. In addition, it contains inherent uncertainty in the toxicity values. However, if the data exists this methodology provides a useful technique for incorporating risk analysis into a waste minimization strategy.

CONCLUSION

In summary, the objective of this work was to develop a strategy for reducing waste in chemical processes through process modification. Although the details of this approach are presented, the purpose of this research is to show how the methodology works and how it can be incorporated into a waste minimization strategy by using process modeling skills and an understanding of the process chemistry.

With promulgation of recent stringent environmental regulations, companies need a methodology that will give both structure and flexibility. This approach provides both, for example, if the waste costs change, the process model can be re-optimized to find the new optimal operating parameters. In addition, it can be expanded to include more source reduction variables in the objective function. Although more processes need to be studied to verify the validity of the approach, its simplicity and ease of use warrant its utility for industrial application.

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LITERATURE CITED

1. **Freeman, H., T. Harten, J. Springer, P. Randall, M. A. Curran, and K. Stone**, "Industrial Pollution Prevention: A Critical Review," *Journal of Air and Waste Management Association*, **45**(5), pp. 619-653 (1992).
2. **Shanley, A.**, "Pollution Prevention: Reinventing Compliance," *Chemical Engineering*, **100**(11), pp. 30-43 (1993).
3. **Kneupper, C. and L. Saathoff**, "Allyl Chloride," in "Kirk-Othmer Encyclopedia of Chemical Technology," J. I. Kroshwitz, ed., 4th ed., Vol. 6, John Wiley & Sons, New York, pp. 59-69 (1993).
4. **Norman, M. E., S. Kapur, G. A. Smalley Jr., and B. M. Daniel**, "Refinery Wastewater—1: U.S. Regulations Cause Refiners to Rethink Wastewater Systems," *Oil and Gas Journal*, **90**(22), pp. 54-64 (1992).
5. **Kovalic, J. M.**, "The Clean Water Act of 1987," Water Environment Federation, Alexandria (1987).
6. *Federal Register*, **59**, p. 19403 (1994).
7. **Biegler, L. T. and R. R. Hughes**, "Process Optimization: A Comparative Case Study," *Computers and Chemical Engineering*, **7**(5), pp. 645-661 (1983).
8. **Hopper, J. R., C. L. Yaws, T. C. Ho, M. Vichailak, and A. Muninnimit**, "Waste Minimization By Process Modification," in "IUCCP Symposium: Waste Minimization in Industrial Processes and Remediation of Hazardous Waste," A. E. Martell and D. T. Sawyer, eds., Plenum Press, New York, pp. 25-43 (1992).
9. **Krahling, L., J. Krey, and G. Jakobson**, "Allyl Compounds," in "Ullmann's Encyclopedia of Industrial Chemistry," W. Gerhartz, ed., 5th ed., Vol. A1, VCH Verlagsgesellschaft, Weinheim, pp. 425-445 (1985).
10. **Smith, J. M.**, "Chemical Engineering Kinetics," 3rd ed., McGraw-Hill, New York (1981).
11. **Freeman, H.**, "Hazardous Waste Minimization," McGraw-Hill, New York (1990).

Reducing the Leachable Lead Content of Used Oil Filter Paper

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Used automotive oil filter papers are typically contaminated with traces of lead and zinc particulates that may exceed the EPA toxicity characterization leaching procedure (TCLP) or the California soluble threshold limit concentration (STLC). The leachable lead and zinc content of oil filter paper may be reduced below hazardous waste levels by treatment with leach solutions comprised of metal complexing agents that dissolve a portion of the heavy metals. Further reduction of leachable lead and zinc in filter paper may be achieved by treatment with phosphate solutions to form insoluble metal phosphates. The resultant non-toxic paper may be safely incinerated, while the leach "solubilizing" and phosphate "fixing" solutions are recycled. Lead and zinc are recovered from leach solutions by precipitation with sodium sulfide or polysulfide for beneficial use in lead/zinc smelter feedstock. The total levelized cost of treatment of filter paper to yield a non-hazardous waste may range from \$100-\$300 per metric ton.

BACKGROUND

The remediation of heavy metal-contaminated soils is currently receiving much attention [1]. Lead, zinc, cadmium and chromium have been found in high concentrations at a number of locations, including many Superfund sites. Soil-washing with acids and metal complexing/chelating agent solutions to solubilize the heavy metals is well-documented [2, 3, 4, 5, 6]. Several processes to remove lead and other heavy metals from soils have been successfully demonstrated at remediation sites [1].

Regulations generated by the federal government [7] and by some state governments [8] govern the classification, handling, and disposal of various types of soils and wastes. For example, when the leachable concentration of lead in a waste equals or exceeds 5.0 mg/L as determined by the EPA Method 1311 Toxicity Characteristic Leaching Procedure (TCLP) or the California Assessment Manual (CAM) Waste Extraction Test (WET), the waste is considered to be hazardous by standards established by both the federal and California State governments. According to CAM, wastes containing total threshold limit concentrations (TTLC) of 1,000 mg/kg lead and 5,000 mg/kg zinc are also classified as hazardous. In addition, when the leachable concentration of zinc equals or exceeds 250 mg/l as determined by the WET procedure, the waste is considered to be hazardous by California standards, the federal government

having not yet established a maximum permissible leachable zinc concentration for non-hazardous wastes.

Such hazardous waste classifications can significantly impact the ability to recycle materials, e.g., used automotive oil filters. These oil filters can be separated into their component parts, namely scrap casing metal, used oil, and oil-contaminated paper. The metal can be reprocessed by smelters for use in other goods, and most of the used oil can be re-refined and recycled. At present, incineration is the most economical technique for handling the oil-contaminated paper. Lead and other heavy metals may be present in oil filter paper at sufficient concentrations to classify the paper as a hazardous material. The lead and heavy metal content of the filter paper should be reduced to allow environmentally acceptable disposal by incineration or landfilling.

EXPERIMENTAL

Samples of used oil filter paper obtained from a southern California recycler were utilized throughout this study. All paper samples were ashed at 490°C, the ash was digested in nitric acid, and the digest solution was analyzed for total lead and zinc by inductively-coupled plasma (ICP) spectrometry. Typically, these paper samples exhibited a total lead concentration ranging from 250 to 1000 mg/kg, and total zinc concentration of 800 to 2250 mg/kg. These analyses were confirmed by x-ray fluorescence spectroscopy of the respective paper samples. The leachable lead content of this paper by EPA Method 1311 that utilizes an acetate buffer is typically < 1 mg/L, but leachates from the California WET STLC test that utilizes a citrate buffer range from 15 to about 30 mg/L. The WET STLC (leachable) zinc content range from 50 to 150 mg/L. Therefore, this used oil filter paper is considered a hazardous waste by California standards with respect to lead.

The source of lead and zinc in the paper is small, heterogeneously-dispersed metallic flecks observed in scanning electron micrographs of the paper (see Figure 1). Energy-dispersive x-ray fluorescence spectroscopy indicates that lead and zinc are present as metallic compounds (possibly surficial oxides) or alloys with iron and nickel that are adsorbed or physically trapped in the paper matrix. A fleck of niobium was also detected in one paper sample. These flecks are assumed to derive from wear of engine parts or the filter casing containing these metals.

The paper used in each series of leaching tests was homogenized, so far as possible, by tumbling and shaking in

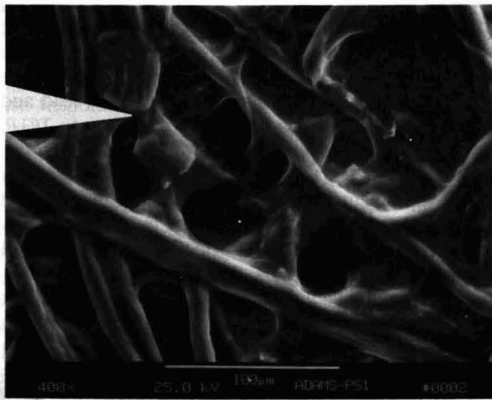
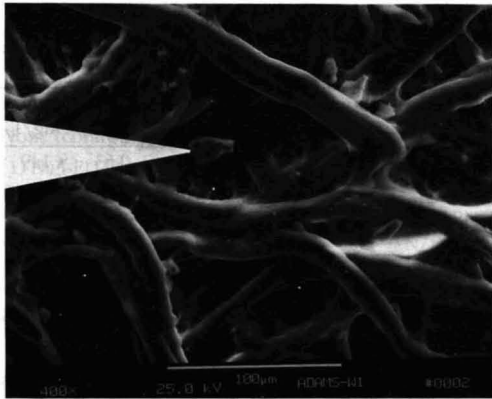


FIGURE 1 Scanning electron micrographs of metal flecks in oil filter paper.

a large glass bottle. A variety of jar tests were conducted in the laboratory to reduce the leachable lead and zinc concentrations in the oil filter paper by chemical solubilization. Generally, in these experiments, ~ 50 g of oil filter paper and ~ 1000 ml of an aqueous leaching solution (solid to liquid weight ratio of ~ 1:20) were placed into

sealed bottles and shaken for 12–24 hours at ambient temperature. The resulting mixtures were filtered through a porous screen (#60 U.S. Screen). The respective filtrates were saved and the leached paper pulp was washed with up to 100 mL of deionized water to remove entrained leach compounds and solubilized metals. Wash waters typically contained < 1 mg/L of lead and zinc. The filtrates and nitric acid digestion extracts of the ashed paper were analyzed by ICP spectroscopy to determine their respective lead and zinc contents. The washed leached pulps were dried overnight in an oven at 75°C and then subjected to the WET and/or TCLP waste characterization procedures by a federal and state-certified environmental testing laboratory. Leachants examined in the study included the complexing and chelating agents, citric acid, acetic acid, sodium acetate buffer, ammonium acetate buffer, nitric acid, ethylenediaminetetraacetic acid (EDTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA), and salts thereof.

Precipitation of lead and zinc from the non-acidic leach solutions was achieved by treatment with sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) or sodium polysulfide (Na_xS_y) solutions. Metal sulfides were recovered from the leach solution by filtration. In one test, a sulfide-treated, sodium-EDTA leach solution was re-used in a leaching test of fresh filter paper. Washing of leached filter paper with sodium hexametaphosphate solution was also examined to determine if lead and zinc could be fixed as insoluble phosphates to reduce the metal solubility in the CAM WET procedure. Metal sulfide concentrates were analyzed by quantitative elemental x-ray fluorescence and x-ray diffraction spectrometry.

RESULTS AND DISCUSSION

Table 1 presents the results of initial leaching tests of a batch of unwashed, homogenized oily filter paper containing 430 and 2,240 mg of lead and zinc, respectively, per kg of paper (control). The control paper was determined to be hazardous with respect to lead according to the CAM WET procedure (STLC, 32 mg/L), but not the TCLP (0.91 mg/L). In this initial series of tests, nitric and citric acids leached sufficient lead and zinc to render the paper non-hazardous according to California regulations. TCLP lead concentrations were assumed to be much less than 0.91 mg/L or the

TABLE 1. Leaching Tests

Leaching Solution	Conc.,		Leachate		Leached Paper		Toxicity Characterization			
	M	pH	Pb,	Zn,	Pb,	Zn,	TTLIC	STLC	TCLP	STLC
			mg/kg	mg/kg	mg/kg	mg/kg	Pb,	Pb,	Pb,	Zn
None (control)	N/A*	N/A	N/A	N/A	430	2240	430	32	0.91	209
Nitric acid	0.5	0.5	15	83	310	990	N/D**	3.1	N/D	20
Citric acid	0.5	3.2	12	58	253	790	N/D	4.1	N/D	20
Acetic acid	0.5	2.1	6.4	58	332	940	N/D	14	N/D	28
Na5-DTPA	0.5	11.4	16	66	120	680	N/D	5.4	N/D	27
Na4-EDTA	0.5	11.9	11	54	304	800	N/D	6	N/D	19
Sodium acetate buffer	0.5	8.5	32	201	132	380	N/D	4.9	N/D	27

* N/A = not applicable; ** N/D = Not determined

TABLE 2. Leaching Tests with Chelant and Detergent / Oxidant

Leaching Solution	Conc., M	pH	Leachate		Leached Paper		STCL	TCLP	STLC
			Pb, mg/kg	Zn, mg/kg	Pb, mg/kg	Zn, mg/kg	Pb, mg/L	Pb, mg/L	Zn, mg/L
None	N/A*	N/A	N/A	N/A	457 (TTLC)	1385	19	0.63	149
Na5-DTPA/Detergent	0.1/100 ppm	11	18	88	340	940	7.8	N/D**	30
Na5-DTPA/H ₂ O ₂	0.1/0.1	10.9	7.7	48	340	1150	8	N/D	30
Na5-DTPA/H ₂ O ₂ /Detergent	0.1/0.1/100 ppm	11.1	13	67	480	1390	7.7	N/D	38

* N/A = not applicable; **N/D = Not determined

reportable detection limit of 0.2 mg/L, and therefore, were not analyzed. By contrast, acetic acid did not yield a non-hazardous paper, but sodium acetate buffered to pH 8.5 performed acceptably. High pH chelating solutions reduced the STLC for lead to near the regulatory criterion limit of 5 mg/L. Leachate and leached paper lead concentrations did not correlate with toxicity characterization STLC results. During leaching of the paper with the high pH solutions, the paper formed a finely-divided pulp that was difficult to separate from the leach solution and was difficult to wash to remove entrained solution and soluble metals. This difficulty in paper washing preparatory to toxicity characterization may be responsible for the lead STLC values slightly exceeding the standard of 5 mg/L.

In a second series of tests, an unwashed oily paper batch contained 457 and 1,385 mg/kg of lead and zinc, respectively. This batch of paper contained nearly the same lead concentration as the initial batch described above, but contained only about half the zinc concentration. Paper samples from this batch were treated with DTPA chelating solution in combination with Rohm and Haas Triton® X-100 non-ionic detergent and/or hydrogen peroxide. Detergent was added to the leaching solutions to determine if heavy metal solubility could be enhanced by converting metal flecks from an oil-wet to a water-wet condition. The oxidizing agent, hydrogen peroxide, was tested to determine

if oxidizing conditions would enhance metal leaching. As shown in Table 2, these combination treatments did not afford a particular advantage in leaching the heavy metals to produce a non-hazardous paper compared to the chelating agent alone.

Additional leaching tests were conducted with chelating solutions at reduced concentration and pH's ranging from 4-8 (see Table 3). The batch of oily paper employed in this series of tests contained 330 and 804 mg/kg of lead and zinc, respectively, was non-hazardous according to TCLP, but was hazardous based on California lead regulations. This batch of paper exhibited a reduced oil content as a result of a change in operation by the recycler. Acetate and citrate solutions did not dissolve sufficient lead in the paper to allow it to pass the STLC. The STLC of 5 mg/L lead was approached by leaching the paper with DTPA-ammonium salt solution adjusted to pH 5.1, EDTA-sodium salt solution adjusted to pH 7.8, and HEDTA-ammonium salt solution adjusted to pH 6.9. At relatively neutral pH, the chelate solutions did not form a fine paper pulp as encountered at high pH. As a result, separation of paper from leach solution filtrate, and washing with water proved to be a much easier operation than in the high pH experiments. Surprisingly, the paper sample treated with a trisodium-EDTA solution that yielded a STLC of 5 mg/L lead, also resulted in a TCLP of 2.7 mg/L, which is three

TABLE 3. Additional Leaching Tests

Leaching Solution	Conc., M	pH	Leachate		Leached Paper		STLC	TCLP	STLC
			Pb, mg/kg	Zn, mg/kg	Pb, mg/kg	Zn, mg/kg	Pb, mg/L	Pb, mg/L	Zn, mg/L
None (control)	N/A*	N/A	N/A	N/A	330 (TTLC)	804	15	0.75	98
Ammonium acetate	0.2	4.1	3.7	80	300	740	17	0.42	17
Sodium citrate	0.2	4.2	10	88	270	680	11	1.1	16
Sodium citrate	0.6	7	8.5	57	240	510	7.3	< 0.4	12
Sodium acetate/citrate	0.1/0.1	4.1	9.4	93	280	700	11	0.59	19
Ammonium DTPA	0.2	4.1	14	85	250	660	7.7	0.42	18
Ammonium DTPA	0.2	5.1	17	100	210	730	5.5	< 0.4	15
Na2-EDTA	0.2	4.8	11.5	25	280	790	9.6	0.43	24
Na3-EDTA	0.2	7.8	16	71	200	630	5	2.7	16
Na4-EDTA	0.2	11.2	14.5	91	240	700	11	0.58	21
Ammonium-HEDTA	0.2	6	14	72	260	760	6.6	0.66	15
Ammonium-HEDTA	0.2	6.9	16	99	220	590	5.4	0.51	17
Ammonium-NTA	0.2	6	13	76	290	640	7.3	1.5	20

* N/A = not applicable.

TABLE 4. Leaching Tests with Recycling and Phosphate Fixation

Leaching Solution	Conc., M		Leachate		Leached Paper		STLC	TCLP	STLC
	M	pH	Pb, mg/kg	Zn, mg/kg	Pb, mg/kg	Zn, mg/L	Pb, mg/L	Pb, mg/L	Zn, mg/L
None (control)	N/A*	N/A	N/A	N/A	705 (TTLC)	1250	33	1	75
(1) Na3-EDTA	0.2	7.5	15	56	600	1040	4.9	0.65	30
Recycled (1) Na3-EDTA	0.2	7	12	82	580	1000	6.9	0.87	26
(2) Na2-EDTA	0.2	5	38	165	620	970	5	0.61	31
(2) Na-Hexametaphosphate	0.05	5	N/D**	N/D	N/D	N/D	3.1	< 0.4	18

* N/A = not applicable; ** N/D = Not determined

times the control value. This result may be explained by sample heterogeneity, entrained soluble lead from unwashed leach solution or the presence of a fleck of lead in the sample portion subjected to the TCLP acetate buffer medium.

In a final series of tests shown in Table 4, experiments were conducted with a batch of oily filter paper containing 705 and 1,250 mg/kg of lead and zinc, respectively. In one test, trisodium-EDTA solution was recycled in the paper leaching process. An initial solution (0.2M, pH 7.5) was contacted against oily paper resulting in a STLC of 4.9 mg/L lead. The tri-sodium EDTA solution was treated with sodium polysulfide to precipitate the heavy metals. The heavy metal sulfides were filtered from the leach solution and washed with deionized water resulting in a solid containing 1.2 wt% lead, 1.9 wt% zinc, 14.6 wt% iron and 46 wt % total sulfur present as galena, PbS, and iron-substituted sphalerite, Fe,ZnS. The leach solution, from which the metal sulfides were recovered, was subsequently contacted against fresh, untreated oily paper. Lead and zinc were leached from the paper by the recycled chelating solution to about the same extent as the original leach test. The resultant paper passed the TCLP for lead, but exceeded the STLC slightly (6.9 mg/L).

Recycling of chelating solutions by sulfide precipitation or electrolysis has previously been shown to successfully leach metal contaminants [9, 10]. Recycling of the trisodium-EDTA solution, *vide supra*, successfully leached additional lead and zinc, as designed. However, subsequent leaching of the paper sample with the recycled solution did not further reduce the leachable STLC lead concentration. This result implies that until the lead is leached from the paper down to ~ 50 mg/kg, with fresh or recycled solutions, the STLC may still be exceeded according to the definition of the WET procedure [8].

Many lead phosphate compounds encountered in nature are extremely insoluble [11, 12]. In an attempt to "fix" leachable or entrained, solubilized lead in the paper, a dual treatment of chelate and phosphate was examined (see Table 4). Oily paper was leached with disodium-EDTA solution resulting in a waste paper that just met the STLC of 5 mg/L lead. After the chelating solution was recovered by filtration, the paper was rinsed with a dilute sodium hexametaphosphate solution. Phosphate apparently formed an insoluble form of lead in the paper, as the resultant STLC of the leached and washed paper was reduced slightly from 5 to 3.1 mg/L lead.

Due to heterogeneities of the samples and the likely uneven dispersion of lead and zinc-containing flecks in the

oil filter paper, it is difficult to obtain mass balance closures for these leaching tests. Some flecks may be especially oil-wet thereby inhibiting the dissolution of metals by the leaching or fixing solutions. Wide variations in test results are attributed to these heterogeneities between samples rather than analytical error. Some consistency in leach results was observed between tests, however. For example, the 0.2 M trisodium-EDTA leach of paper containing 330 mg/kg lead at pH 7.8 in Table 3 yielded 16 mg/L lead. The lead STLC was 5 mg/L, and the leached paper contained 200 mg/kg lead, a decrease of 130 mg/kg or 39%. By comparison, treating paper containing 705 mg/kg lead with fresh 0.2 M trisodium-EDTA at pH 7.5 in Table 4 resulted in a leachate containing 15 mg/kg lead. The lead STLC and TTLC of the leached paper was 4.9 mg/L and 600 mg/kg, respectively. The lead in the paper decreased by 105 mg/kg or 15%.

CONCEPTUAL PROCESSES FOR TREATING OIL FILTER PAPER

The results of this laboratory study suggest that a leaching process for reducing the leachable lead content of oil-contaminated paper to less than 5.0 mg/l, thus enabling the processed paper to be incinerated or disposed as a non-hazardous waste, is feasible. A conceptual process is envisioned, which would typically be conducted in a batch or semi-continuous mode. The process comprises of contacting the lead-contaminated paper with a leaching composition (preferably a dilute chelating solution) to form a slurry in a stirred tank reactor. Prior to leaching, the filter paper is separated from its metal casing and the bulk of the waste oil is squeezed therefrom in a pressing operation. A diagram of the process to reduce the lead, and other heavy metal-leachable content of oil filter paper is shown in Figure 2.

The leaching solution is typically comprised of an aqueous solution consisting of metal-complexing agents. Examples of these agents include acetic acid, citric acid, buffers of the foregoing acids, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, nitrilotriacetic acid, and possibly mixtures thereof. Alkali metal or ammonium salts of the chelating agents (EDTA, DTPA, etc.) may be employed provided the solutions are maintained at a relatively neutral pH (4-8). In these neutral forms, the chelate leach solutions are preferred because they can be easily recycled in the subsequent steps of the process, they are easy to handle, and they allow easier mechanical separation of the paper/leachate slurry. The solute in the leach solution may vary in concentration. The results of this study suggest

to ensure that substantially all the sulfide-precipitable metals present therein have been precipitated as sulfides. The end point of this precipitation process may be determined, for example, by monitoring the turbidity in the precipitation tank or analyzing the solution for heavy metals.

Specifically, when the measured turbidity or metals concentrations remain substantially unchanged with an incremental addition of the sulfide-containing compound, most of the leached metals should have precipitated, and there is no need for further addition of the sulfide-containing compound.

The precipitated metal sulfides form a floc that settles rapidly. The heavy metal-containing precipitate is separated from the leach solution as heavy metal concentrate by thickening and/or filtration. The filtered concentrate may be further washed with water to remove leachant and the metal precipitate is dried. The dried metal precipitate may potentially be beneficially used as feedstock to a smelter or disposed by a metal's recycler.

The leachate recovered from the metal precipitation step may be recycled to the leaching tank. Typically, the leachate should be recycled as many times as possible before being discarded. After spending, the leachate leaving the metal precipitation tank may be disposed (if it proves to be a non-hazardous liquid) or sent to a metal/leachant recycler.

Leached paper pulp may also be washed with a dilute solution of sodium phosphate as a means of fixation of metals as insoluble phosphates, i.e., lead and zinc phosphates. This fixation process inhibits lead and zinc from leaching in citrate and acetate buffer solutions employed in waste toxicity characterization testing procedures. The phosphate wash solution may also be recycled, preferably as many times as possible.

The leached paper, washed with water or phosphate solution, may be sent to a drier to reduce waste weight. Once the dried paper exiting the drier exhibits a leachable lead content of less than 5.0 mg/l (as determined by the TCLP and WET procedures), it may be handled as a non-hazardous waste and disposed of accordingly, e.g., incineration in kilns or heaters, or landfilling.

OIL FILTER PAPER DE-TOXIFICATION PROCESS EXAMPLE

Table 5 presents a conceptual example of a paper detoxification process that treats 1000 kg per day of representative oily paper from the southern California recycling operation. In this example, approximately 7.6 m³ of 0.2 M disodium-EDTA leach solution is slurried with the paper at ambient temperature for 18 hours. In concept, the leach solution is recycled at least ten times before being discarded, although no testing has been conducted to demonstrate this potential usage. Lead and zinc sulfide concentrates (20–25 kg) are recovered from the leach solution and the solid byproduct is sent to a smelter. Anticipated chemical operating costs of the process are included in Table 5, together with an equipment list summary. It is estimated that the total levelized capital and expense cost to treat one metric ton of paper may range from \$100–\$300.

CONCLUSIONS

Paper retrieved from used oil filter recycling operations may contain significant leachable lead and other heavy

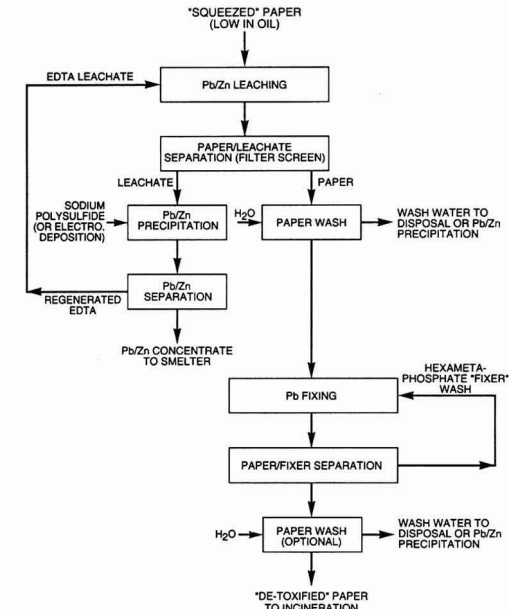


FIGURE 2 Filter paper detoxification process flow diagram.

that complexing agent concentrations of about 0.1–0.5 M will leach sufficient heavy metals from this particular recycler's paper to yield a non-hazardous waste.

The leaching composition and filter paper generally need to be contacted in the stirred tank reactor at a ratio of up to about 20:1 (weight of the aqueous, liquid, leaching composition to the weight of the oily, metal-contaminated paper) to obtain satisfactory results. The paper is stirred in the reactor with the leaching composition for an amount of time required to achieve a stabilized, maximum leachable lead concentration. Leaching may be repeated as necessary until the remaining leachable lead content of the paper is expected to be less than 5 mg/l when the paper is subsequently separated and subjected to either the TCLP or WET procedures. On the basis of the paper used in this study, the optimum leaching time typically ranges from 12–24 hours under gentle agitation conditions.

The leach solution reacts with lead, zinc and other heavy metals in the paper to form water-soluble complexes. Lead and other heavy metal contaminants are preferably leached from the oily paper by chelating agents to render the paper waste non-hazardous. Upon completion of the contacting or leaching step, the slurry is separated into a liquid leachant phase and a solid paper pulp phase using a filter mechanism. Preferably, the filter employed has a U.S. sieve series number of about 10 to about 100. After separation, the leached paper may then be washed with water to remove entrained leachate.

The separated leach solution is transported to a holding tank or clarifier, and then contacted with sodium sulfide or sodium polysulfide solution to reduce the water-soluble, heavy metal content of the liquid by forming heavy metal sulfide precipitates. A very slight excess of the sulfide-containing compound dissolved in water must be introduced into the metal precipitation tank under agitative conditions

TABLE 5. Simplified Process Operations Costs

Operation	
PAPER LEACHING	
Paper Load	1000 kg/day
Paper: Leach Solution (wt. basis)	1000 kg: ~ 8 cubic meters
Leach Solution:	0.2 M Na ₂ -EDTA
Na ₂ -EDTA	560 kg
Water	7350 L
Leach Time	18 hours
Leachate Loading:	
Lead	0.1 kg
Zinc	0.2 kg
Leach Solution Storage Tank	10 cubic meter capacity with stirrer
Leach Reaction Tank	10 cubic meter capacity with stirrer
SLURRY SEPARATION	
Wash Water*	Filter press or screen
	7350 L
Wash Water Storage Tank	10 cubic meter capacity
*Optional Phosphate Wash	0.01 M; 7350 L
(NaPO ₃) ₆	46 kg in 7350 L water
METAL RECOVERY (1 cycle per day)	
Lead Leachate Loading	0.1 kg
Zinc Leachate Loading	0.2 kg
Sodium Polysulfide	.3 kg
Metal Concentrate	2.3 kg
Concentrate Clarifier/Thickener	10 cubic meter capacity
Filter Press	
Wash Water	190 L
Concentrate Storage Bin	
PAPER DISPOSAL	
Drier	1000 kg/day capacity
Storage Bin	1000 kg/day capacity
COSTS, \$	
Chelate (minimum 25 cycles)	\$21/day
Sodium Polysulfide	\$2/day
Metal Concentrate Value	(\$2/day)
Total	\$21/day

metals. The paper may be classified as a hazardous material as a result of leachable metal concentrations. The present study has shown that lead and zinc can be leached from oil filter paper by complexing/chelating agents in a relatively simple process. Lead and zinc concentrations in the paper may be leached sufficient to render the paper non-hazardous according to federal and California waste regulations. Paper that is de-toxified may be safely disposed or incinerated for heat value. Lead, zinc and other heavy metals may be recovered in this process for possible use as smelter feedstock.

ACKNOWLEDGMENT

I thank Unocal Corporation management for permission to publish the results of this study.

NOTATION

TCLP = Toxicity characterization leach procedure
 TTL = Total threshold limit concentration

STLC = Soluble threshold limit concentration
 CAM = California Assessment Manual
 WET = Waste extraction test (California)
 EDTA = Ethylenediaminetetraacetic acid
 HEDTA = (2-Hydroxyethyl)ethylenediaminetriacetic acid
 NTA = Nitritoltriacetic acid
 DTPA = Diethylenetriaminepentaacetic acid
 M = Molarity, moles/liter

LITERATURE CITED

1. **G. Parkinson**, "Recovering Metals from Wastes," *Chem. Eng.*, 30-33 (April 1994).
2. **C. Castle, J. Bruck, D. Sappington, and M. Erbaugh**, "Research and Development of a Soil Washing System for Use at Superfund Sites," *6th Intern. Conf. on Management of Uncontrolled Hazardous Waste Sites*, 452-455 (1986).
3. **R. W. Peters and L. Shem**, "Use of Chelating Agents for Remediation of Heavy Metal Contaminated Soil," pp. 70-84 in *ASC Symp. Series 509, Environmental*

Remediation: Removing Organic and Metal Ion Pollutants, G. F. Vandergrift, D. T. Reed and I. R. Tasker, Eds., Washington, D.C. (1992).

4. **J. C. O'Shaughnessy, R. A. D'Andrea, M. R. Canniff, T. J. St. Germain, S. Venkataramanappa, and M. J. Macaulay**, "Evaluation of In Situ Soil Flushing Techniques for Heavy Metals Removal from Contaminated Soils," pp. 123-139 in *Proc. 48th Industrial Waste Conference*, Lewis Publishers, Boca Raton, FL (1994).
5. **R. W. Peters and L. Shem**, "Adsorption/Desorption Characteristics of Lead on Various Types of Soil," *Env. Prog.*, **11**,(3) 234-240 (1992).
6. **B. E. Holbein and D. K. Kidby**, U.S. Patent 5,342,449 (1994).
7. **Federal Register**, Title 40 Code, 260-272 (1994).
8. **California Code of Regulations**, Division 4.5, Chapter 11, Appendix II as set forth in Barclays Official California Code of Regulations, Title 22. Social Security, Division 4.5 Environmental Health Standards for the Management of Hazardous Waste, Volume 29A, Barclays Law Publisher, South San Francisco, CA (1991).
9. **M. Ghassemi**, "In Situ Technologies for Vadose Zone Remediation," pp. 1-40 in Vol. 4, *Encyclop. of Env. Control Tech.*, P. N. Cheremisinoff, Ed., Gulf Publishing, Houston, TX (1990).
10. **H. E. Allen and P-H. Chen**, "Remediation of Metal Contaminated Soil by EDTA Incorporating Electrochemical Recovery of Metal and EDTA," *Env. Prog.*, **12**(4), 284-293 (1993).
11. **J. O. Nriagu**, in *Phosphate Minerals*, J. O. Nriagu and P. B. Moore, Eds., Springer-Verlag, New York (1984).
12. **M. V. Ruby, A. Davis, and A. Nicholson**, "In Situ Formation of Lead Phosphates in Soils as a Method to Immobilize Lead," *Environ. Sci. Technol.*, **28**(4), 646-654 (1994).

MEMBERSHIP APPLICATION

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Check grade (and Graduate Student Status if applicable) see over for requirements

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(Last) (First) (MI)

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Company: _____

Position/Dept: _____

Street: _____

City: _____ State: _____ Zip: _____

Co. Tel: _____ Home _____

Date of Birth: (Mo) _____ (Day) _____ (Yr) 1 9 _____ Sex: F M

GRADUATE STUDENT STATUS

Graduate student status is available within each grade. Full time graduate students employed below the rank of instructor may request graduate status and receive reduced dues by completing the following:

Yes, I am a full time graduate student. In addition to the grade selected above, place my name on your graduate records

Name of Univ. or College _____

Expected Degree _____ Major _____ Grad Date _____

EDUCATION

NAME OF COLLEGE OR UNIVERSITY	DEGREE	MAJOR	DATE OF DEGREE
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

PROFESSIONAL EXPERIENCE (Attach additional information, if necessary)

Employer _____ From Year _____ To: Present

Address _____

Your Job Title _____	Chemical Engineering Experience
	Yrs. _____ Mos. _____

Nature of Your Duties & Responsibilities Related to Chemical Engineering: _____

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Year of graduation

Before 1991	\$125	Graduate Student	\$25
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Card Holder Signature _____

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Total: _____

* Copy of degree(s) must be attached. If no degree check here

APPLICANT'S SIGNATURE

I, the undersigned, attest that the statements I have given are true. If elected to membership, I agree to abide by the Constitution, the Code of Ethics and the Bylaws (see over) of AIChE.

Signed: _____ Date: _____

BOX FOR OFFICE USE ONLY

Member #:	Ap'l #	Ap'l Grd	Source Code:	PRIZE DRAWING COUPON	CEP
	Committee:		Status:		
				Sponsor (if available): _____	
				Sponsor Member # _____ Applicant's Name _____	

REQUIREMENTS FOR MEMBERSHIP

CONSTITUTION (a)

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.

(a) From the AIChE Constitution as amended to April 1, 1989

BYLAWS (b)

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.

MEMBERSHIP REQUIREMENTS CHART

EDUCATION	YEARS OF WORK EXPERIENCE IN CHEMICAL ENGINEERING		
	Affiliate	Associate	Member
An earned degree in chemical engineering from a school of recognized standing	Bachelor 0 Master 0 Doctoral 0	0 0 0	4 3 2
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*	6 5 4
An earned baccalaureate degree in natural science or in engineering other than chemical engineering from a school not of recognized standing	0	2	6
An earned baccalaureate degree in a field other than engineering or natural science	0	5	8
No degree	0	5	9

(*) Must be currently practicing chemical engineering.

(b) From the AIChE Bylaws as amended to November 8, 1993.

CODE OF ETHICS

Members of the American Institute of Chemical Engineers shall uphold and advance the integrity, honor and dignity of the engineering profession by: being honest and impartial and serving with fidelity their employers, their clients, and the public; striving to increase the competence and prestige of the engineering profession; and using their knowledge and skill for the enhancement of human welfare. To achieve these goals, members shall

1. Hold paramount the safety, health and welfare of the public in performance of their professional duties.
2. Formally advise their employers or clients (and consider further disclosure, if warranted) if they perceive that a consequence of their duties will adversely affect the present or future health or safety of their colleagues or the public.
3. Accept responsibility for their actions and recognize the contributions of others; seek critical review of their work and offer objective criticism of the work of others.
4. Issue statements or present information only in an objective and truthful manner.
5. Act in professional matters for each employer or client as faithful agents or trustees, and avoid conflicts of interest.
6. Treat fairly all colleagues and co-workers, recognizing their unique contributions and capabilities.
7. Perform professional services only in areas of their competence.
8. Build their professional reputations on the merits of their services.
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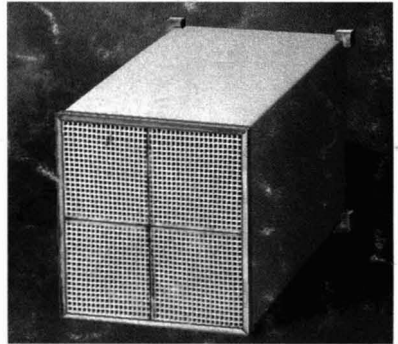
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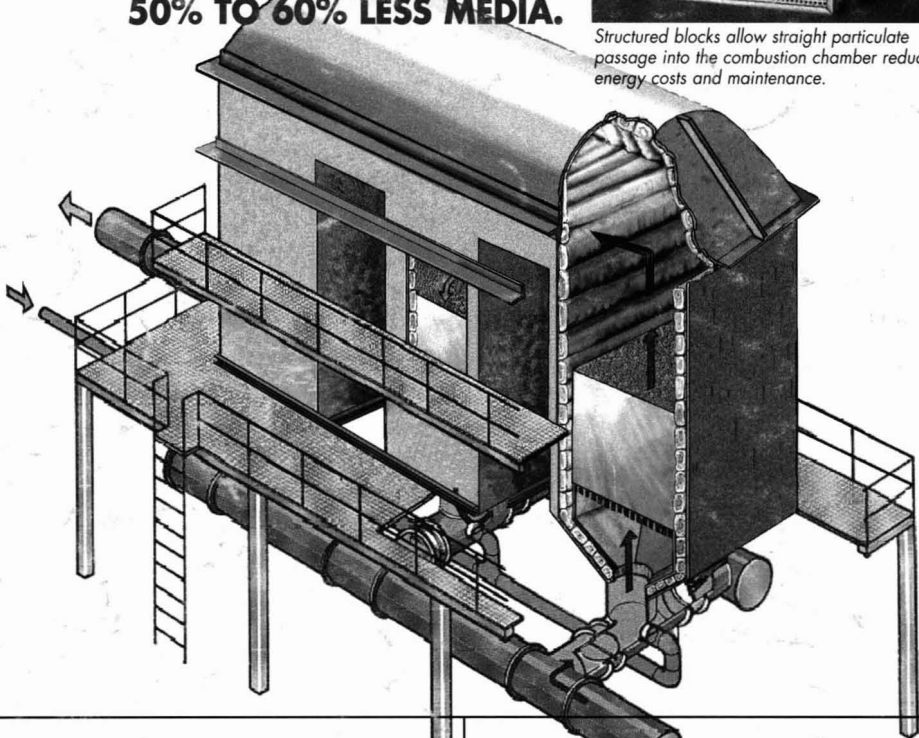
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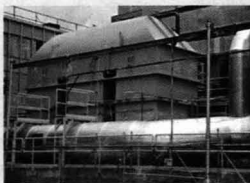


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