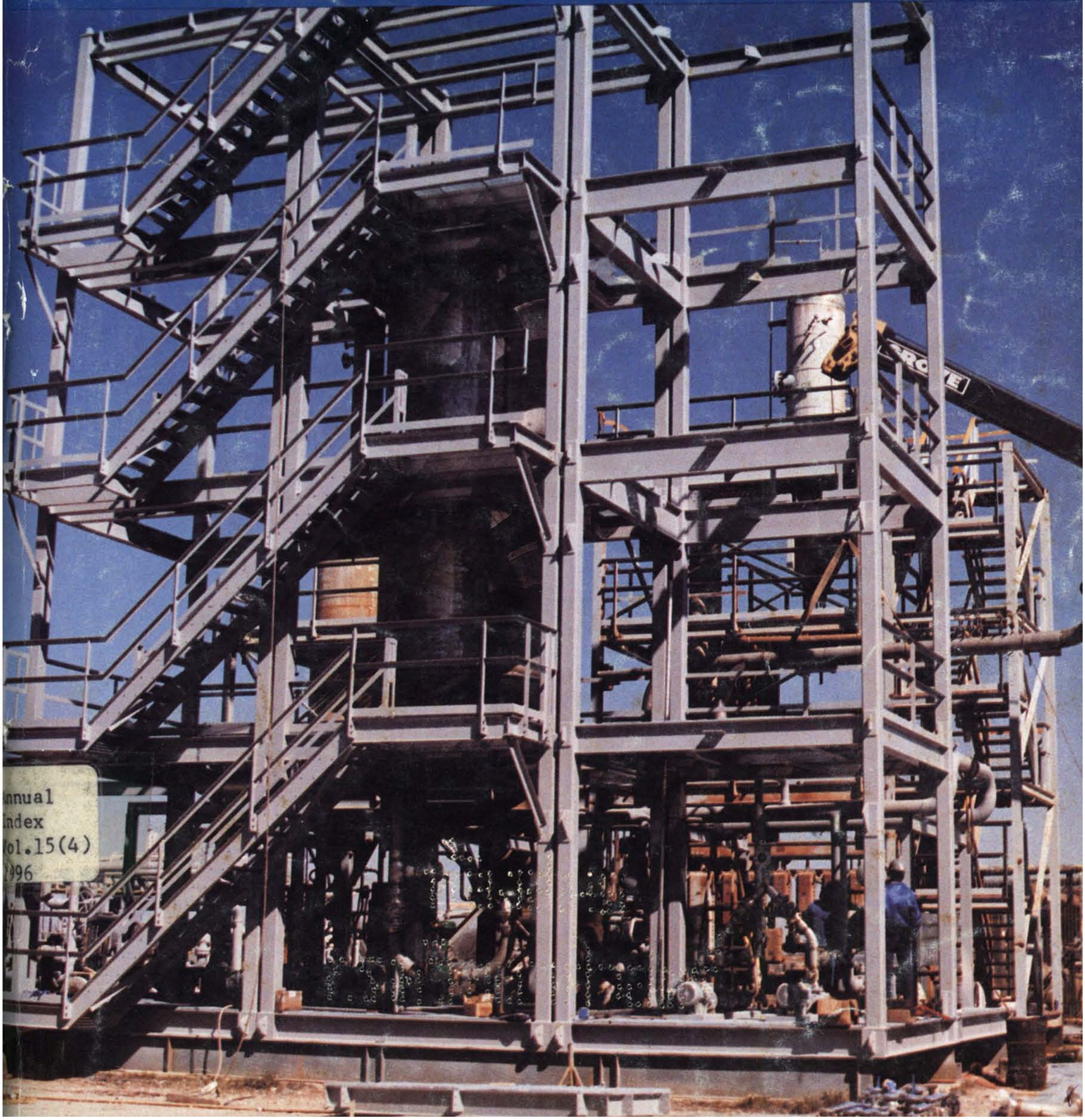
ENVIRONMENTAL PROGRESS

Vol.15 No.4 Winter 1996



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, presents a 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

Nearly all of the recommended R&D activities are expected to produce significant results within ten years. And nearly half of the R&D activities proposed will provide results in three years or less.

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

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Published four times a year (February, May, August, and November) by the American Institute of Chemical Engineers, 345 E 47th St., New York, N.Y. 10017 [ISSN 0278-4491]. Manuscripts should be submitted to the Manuscript Center, AIChE 345 E 47th St., New York, N.Y. 10017. Statements and opinions in *Environmental Progress* are those of the contributors, and the American Institute of Chemical Engineers assumes no responsibility for them. Subscription price per year $185. AIChE Environmental Division Members $40 included in dues. Outside the U.S. please add $30 per subscription for postage and handling. Single copies $55. Outside the U.S. please add $6 for postage and handling. Payment must be made in U.S. dollars. Periodicals postage paid at New York, N.Y. and additional mailing offices.
Environmental Progress fee code: 0278-4491/96 $3.50.
Postmaster: Please send change of addresses to *Environmental Progress*, AIChE, 345 E 47th Street, New York, N.Y. 10017.

Cover: Modular construction of a Dow Chemical SulFerox unit at Westfield Engineering and Services Company in Houston, Texas (see story on page W5). Photo courtesy of Dow Chemical Company.

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Brownfields Initiatives: Progressive Approach to Solving Urban Environmental Problems

Ira L.Whitman

The Whitman Companies Inc., 44 West Ferris Street, East Brunswick, N.J. 08816

Brownfields site restoration is one of the most constructive and positive elements of national environmental policy to have been developed in a decade. EPA is promoting the restoration and redevelopment of abandoned urban industrial sites with its National Brownfields Pilot Demonstration Programs. Through these programs, EPA has funded over 60 grants to local government agencies to assist them in developing the resources with which to facilitate Brownfield restoration. Recycling contaminated urban industrial land back into productive use is a win-win proposition for the environment and for the economy.

As the 1996 Kappe Lecturer for the American Academy of Environmental Engineers, I have been visiting university campuses across the country giving two lectures on Brownfields. The first is a technical presentation entitled "Engineering the Remediation of Brownfields Sites: Solving the Environmental Problems Created by Urban Industrial Land Use." The second presentation, nontechnical in nature , is entitled "Industrial Site Restoration, The Diversity of Interests." These lectures have been illustrating, to an enthusiastic audience of university students, many of the engineering and legal concepts that are now being adopted to make Brownfield restoration a practical reality.

Current legislation in many states is creating the legal basis for state governments to eliminate the liability to new property owners for past incidence of environmental contamination. Indemnification for new purchasers of commercial and industrial real estate intending to restore and redevelop the abandoned properties eliminates one of the principal impediments to the reuse of abandoned industrial sites.

State regulatory agencies have created so-called "voluntary cleanup programs" to facilitate the investigation and remediation of contaminated Brownfield sites. The regulatory basis of most of these programs includes risk-based cleanup standards for soil, ground water and building surfaces, the use of engineering and institutional controls in lieu of permanent cleanup remedies, and the reclassification of ground water zones in urban areas where no potable water supplies are affected. The key to the success of voluntary cleanup efforts for Brownfield sites is to tie *future use* of the property and its surrounding environs to the environmental condition and remedial approaches designed to protect against the *risks of environmental hazards.*

Capping urban sites through construction of an impermeable barrier at the surface provides an engineering control approach that is cost effective, environmentally sound and in concert with the future use of the Brownfield property. Source removal in lieu of ground water remediation makes sense for aquifers that are affected by a wide array of industrial and urban contaminant sources and are unusable as a potable water resource.

Because Brownfields restoration is good for the environment *and* good for the economy, and therefore is good for the future of our cities, I have been advocating the aforementioned elements of voluntary Brownfields cleanup programs, and other *practical* approaches to eliminating the economic and environmental blight of abandoned industrial sites. However, I do not advocate across-the-board rollback of environmental standards, nor do I believe that subjecting environmental regulations to arbitrary and artificial cost-benefit criteria is good for either the economy or the environment.

Flexible application of environmental rules, and the use of risk assessment in concert with the application of environmental standards give us valuable tools in managing our resources and in restoring abandoned industrial sites. Weakening environmental legislation on the other hand, such as was proposed in the Clean Water Act Amendment, H.R. 961, in 1995, is a disservice to the public and to the dedicated environmental professionals who have accomplished so much with the implementation of several generations of complex legislation.

The immense progress we have made in 25 years by providing cleaner air and water should not be reversed by lawmakers who perceive environmental quality as retarding economic growth. We cannot have a vibrant economy without a healthful and clean environment. Brownfields restoration - definitely; environmental rollback - definitely not!

***Ira L. Whitman, Ph.D., P.E.**, is President and Principal Consultant of The Whitman Companies, Inc., specialists in Environmental Engineering and Management. Prior to going into consulting, Dr. Whitman served as the first Director of the Ohio Environmental Protection Agency. He has helped to guide a national effort on Brownfields through the Northeast Midwest Institute in Washington, D.C., as a member of the Institute's Board of Directors. In addition, he has served in an expert capacity on numerous cases involving environmental compliance and site remediation. He has devoted considerable attention to the problems of redeveloping urban industrial sites, and the risks and economic benefits associated with site reuse.*

He received his B.C.E.,degree in Civil Engineering at The Cooper Union, New York; his M.S. in Civil Engineering at the Polytechnic Institute of Brooklyn, New York; and his Ph.D., in Environmental Engineering Science, at the Johns Hopkins University, Baltimore, Maryland. He is a registered Professional Engineer in six states.

Dr. Whitman is currently involved in advising groups at the U.S. Environmental Protection Agency, The New Jersey Institute of Technology, and several municipalities on Brownfields issues. He was selected to be the Kappe Lecturer of the American Academy of Environmental Engineers for the 1996 Fall Series based on a series of lecturers on the subject of Brownfields which he developed.

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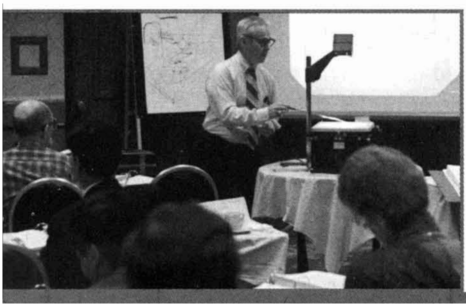

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AIR POLLUTION CONTROL COURSE SLATED FOR NEW ORLEANS IN FEBRUARY

AIChE's Educational Services Department is offering a course on Fundamentals and Technology of Air Pollution Control at the Hotel Monteleone in New Orleans from February 16th through 19th, 1997. The course aims to impart to engineers and scientists an understanding of how to apply current air pollution regulations to monitoring methods, calculational techniques, and design methods for the preservation of air quality management.

Engineers needing a broad view of all the technical aspects of air pollution control, as well as supervisors having responsibility for monitoring compliance with air pollution regulations will benefit particularly, according to AIChE.

Each part of the two-unit course is two days in length. The units, entitled "Air Pollution 1 - Legislation, Measurement and PSD Analysis" and "Air Pollution 2 - Technology of Air Pollution Control" may be taken separately or as a complete two-unit course.

The cost of each unit is $845 to AIChE members, and $945 for nonmembers. For more information or to register please contact the AIChE*xpress* Service Center at 1-800-AIChemE (1-800-242-4363); fax (212) 705-8400; e-mail xpress@aiche.org.

PROCESS RECOVERS SULFUR AT STEEL PLANT

A SulFerox tail treating unit to convert hydrogen sulfide to moist sulfur cake recently begun operating at a steel manufacturing facility near Pittsburgh. This is the first time a SulFerox unit has been used for this type of application. The new SulFerox unit (pictured on the cover of this issue) recovers 6 ton/d.

The SulFerox process is a technology licensed by the Gas/Spec Technology Group of Dow Chemical, for a variety of hydrogen-sulfide removal applications. These applications include refinery and natural gas treatment, geothermal streams, carbon dioxide stream cleanup, vent gases and a variety of chemical process streams.

Operators at Neville, Pennsylvania chose the SulFerox unit for this application to comply with regulatory requirements for hydrogen sulfide removal. Tail gases from a coke manufacturing unit flow to the SulFerox unit where the acid gas is converted to sulfur.

The SulFerox process uses an iron chelate solution to convert hydrogen sulfide to elemental sulfur in a one step process. The sulfur is removed from the process with a filter press to minimize the amount of moist sulfur that is produced. The iron chelate is then recirculated and reused. The unit is modular in design and the skids can be taken apart for shipment.

LATEST PEP SERIES TITLE DEALS WITH ENVIRONMENTAL ISSUES

The Environment: Air, Water, and Soil, published this month by AIChE, is the first in the PEP (Practical Engineering Perspectives) series dealing with environmental issues. Presenting 42 articles describing the best air, water, and soil remediation strategies developed "in the field" over the past five years, the book offers a detailed look at existing and emerging "end-of-pipe" cleanup technologies within each environmental media, as well as methods for waste reduction and/or elimination.

The opening section on air pollution, consisting of 24 papers, reflects the tremendous amount of activity in this field as a result of the Clean Air Act Amendment of 1990. It focuses on developing an emission inventory, reducing VOC and NOx emissions through process or equipment modifications, mapping effective odor control strategies, and selecting an emissions monitoring system.

The 11 water and wastewater treatment articles explore stormwater management, reducing effluent toxicity, and the use of steam strippers and carbon adsorption for the removal of contaminants. Lastly, seven papers look at effective site remediation technologies, including bioremediation, soil vapor extraction, and soil washing.

The Environment: Air, Water and Soil [ISBN 0-8169-0713-7]consists of 320 pages, hardcover. U.S. List Price:$85; International $120.

For more information or to order a copy please call the AIChE*xpress* Service Center at 1-800-242-4363;fax: (212)705-8400; e-mail xpress@aiche.org.

104th Congress Completes Work With Mixed Environmental Record

Prepared by AIChE's Government Relations Staff:

Dale E. Brooks and Sean Devlin Bersell

The Republicans leading the 104th Congress, which ran from January 1995 to October 1996, came to Washington with a vision of reformulating federal environmental policy. Their goal was to bring about what Speaker of the House Newt Gingrich (R-GA) called a "sound, rational, scientifically based and economically affordable environmental policy" and what their opponents called a rollback of a quarter-century of environmental progress. Congressional Republicans sought to effect their environmental policy by rewriting federal laws, nullifying specific regulations, decreasing funding for the U.S Environmental Protection Agency (EPA) and other regulatory agencies, and revising the process for developing regulations.

The Congressional Republicans' attempts to implement their vision were stymied early on, however, when broad-ranging regulatory reform legislation, a comprehensive rewrite of the Clean Water Act, reductions in EPA's budget, and legislative riders addressing a host of environmental issues were blocked by strong opposition from Congressional Democrats and the White House and the public perception that the Republicans were overreaching. Chastened, Congressional Republicans in 1996 avoided polarizing battles over the environment and focused on enacting environmental legislation on which there was broad agreement.

Thus, in spite of the rhetorical battles, the 104th Congress did leave Washington with a number of environmental achievements on its record. The major environmental accomplishments were the passage of a Safe Drinking Water Act reauthorization and enactment of the Food Quality Protection Act. In addition, many minor changes were made to environmental laws. Much remained undone, however, such as the Superfund, RCRA, and Clean Water Act reauthorizations. The 105th Congress, which will convene in January, and will continue to be led by Republicans, will have to decide whether to attempt comprehensive changes in the nation's environmental laws, thus risking reigniting the difficult battles of 1995, or to continue where it left off this year, focusing on a limited agenda of those issues on which there is general consensus.

The following summarizes the activities of 104th Congress on the major environmental issues:

EPA APPROPRIATIONS

The first EPA funding bill prepared by the 104th Congress would have reduced the agency's funding for fiscal year 1996 from $6.6 billion to $5.7 billion. President Clinton vetoed the bill because of the cuts in EPA's programs and because the bill contained several policy "riders" (extraneous non-funding provisions) that would have restricted EPA's ability to implement or enforce several environmental laws and regulations.[1] Following a prolonged debate over the entire federal budget that included two government shutdowns, the Congress and the President finally agreed to provide EPA $6.5 billion in fiscal year 1996. The final bill dropped most of the policy riders.

In fiscal year 1997, to accommodate the president's demands, EPA was provided with $6.7 billion in funding, an increase of approximately 2% over FY 1996.

BUDGET PLANS

The Congress and the President agreed to balance the federal budget by 2002, but the two sides have yet to agree on how a balanced budget will be achieved. Eliminating the budget deficit will require substantial changes in federal entitlement programs and steady cuts in domestic discretionary programs over the next six years, which means overall environmental funding will likely remain constant or decline for the foreseeable future.

BATTERY RECYCLING

Public Law 104-142, enacted in the Spring of 1996, promotes the recycling of rechargeable batteries by exempting them from EPA's hazardous waste requirements. Under the new standards, which address labeling, collection, storage, and transportation, nickel-cadmium batteries will not be considered hazardous waste subject to Subtitle C of the Resource Conservation and Recovery Act; rather, they will be handled under EPA's universal waste rule standards, and collectors and recyclers will not need a RCRA permit. The law also phases out the use of mercury in alkaline batteries. Domestic manufacturers have already stopped using mercury in household batteries, but it is still used in batteries for certain military, medical, and other equipment.

CLEAN AIR ACT

Although a number of bills to amend the Clean Air Act were introduced, Congress made few changes to the law. The most significant change, enacted late last year (Public Law 104-59), altered the law's "employee commute options" from a mandatory requirement to allow states to decide for themselves whether to enforce it. In addition, Congress prohibited EPA from penalizing states that adopt decentralized inspection and maintenance programs.

The major developments regarding the Clean Air Act occurred not in Congress, but in the courts and EPA. In the Spring of 1995, a federal appeals court ruled that EPA exceeded its authority when it issued a rule requiring that 30% of the oxygenates used in reformulated gasoline come from renewable sources such as ethanol. In June of this year, EPA announced its intention to issue a combined proposed rule for clean air

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[1] For more detail on the riders, please see the "Washington Environmental News", *Environmental Progress*, **14**,N5-N6 (November 1995), and *Environmental Progress*, **15**, S7-S9 (Spring 1996).

standards for ozone and particulate matter. In response, while allocating $19 million for research on particulate matter, Congress included language in a report accompanying the EPA appropriations act stating that it believes the current particulate matter standard to be sufficient.

CLEAN WATER ACT

The House of Representatives approved a rewrite of the Clean Water Act (H.R. 961) in May of 1995. The bill would have required risk and cost-benefit analyses for major new clean water regulations, provided greater flexibility in enforcing the Clean Water Act's discharge standards, and loosened restrictions on the development of lands designated as "wetlands." The Senate did not act on the measure, which faced strong opposition from President Clinton and the environmental community. While the sponsors of the bill claimed that it would "provide a flexible, scientifically sound, and cost-effective basis on which to maintain and continue improvements in water quality," the bill's opponents, who dubbed the bill the "dirty water act," argued that H.R. 961 would severely weaken existing water quality safeguards.

PESTICIDES/DELANEY CLAUSE

Congress passed and the President signed the Food Quality Protection Act, legislation to overhaul laws regulating the use of pesticides in raw and processed food (P.L. 104-170). The legislation modifies the controversial "Delaney Clause" to impose a single, health-based standard for both raw and processed foods, allowing for government approval of foods containing minute traces of pesticide residues only if there is a "reasonable certainty" of no harm to consumers from exposure. Prior to the passage of this bill, the Delaney Clause had prohibited any traces of cancer-causing pesticides on processed foods, but the law provided little protection against pesticide residues on raw food. The Food Quality Protection Act also includes provisions on chemical screening for estrogenic effects, community right-to-know, and consideration of the benefits of pesticide use when making safety decisions.

Subsequent to the passage of the act, however, Congress directed that the National Academy of Sciences conduct a two-year study of the human health effects of chemicals that allegedly disrupt the endocrine system, and precluded EPA from developing a chemical screening program until it has the opportunity to review the NAS study. This provision, which was included in the EPA appropriations bill, could impede the development of the chemical screening program for estrogenic effects.

RCRA

Several bills to make major revisions to the Resource Conservation and Recovery Act (RCRA) were introduced in the 104th Congress, but were not enacted. The measures sought to exempt certain low-level wastes from RCRA's hazardous waste requirements, permit EPA to establish flexible waste-management rules based on how waste is handled, and exempt remediation wastes from RCRA in certain circumstances.

However, several minor changes were made during this Congress. One addressed the need for permits for decharacterized wastes disposed of in injection wells and surface impoundments, and relaxed groundwater monitoring requirements for small municipal waste landfills in dry and remote areas (P.L. 104-119). Another exempted rechargeable batteries from RCRA's hazardous waste requirements (P.L. 104-142).

RISK ASSESSMENTS

One of the most heated debates of the 104th Congress surrounded "regulatory reform" legislation, which included provisions on risk assessments. Early in 1995, the House of Representatives passed the "Risk Assessment and Cost-Benefit Act of 1995" (H.R. 1022), which would have required every major federal rule designed to protect the environment, human health, or safety to be accompanied by a risk assessment and a cost-benefit analysis. Similar legislation (S. 343) was debated in the Senate, but proponents were blocked from bringing the measure to a final vote. Last fall, the supporters of regulatory reform legislation tried to enact a stripped-down version of the bill by adding it to unrelated legislation, but the President vetoed the bill in which it was included. Although comprehensive risk assessment legislation was not enacted in this Congress, several bills, such as the Safe Drinking Water Act reauthorization and the Food Quality Protection Act, included provisions requiring a consideration of risk factors when making regulatory decisions.

SAFE DRINKING WATER ACT

The major environmental achievement of the 104th Congress was the enactment of a bill to reauthorize the Safe Drinking Water Act (P. L.104-182). The new law requires the use of risk and cost-benefit analyses in setting drinking water standards, focuses the act on regulating the contaminants of greatest concern, allows greater flexibility in setting standards, prohibits the application of a cost-benefit analysis to the proposed standard for contaminants that result from the treatment of drinking water, and creates a $7.6 billion revolving fund to help states to comply with the act.[2]

SUPERFUND

Although reform of the Superfund law was high on the agenda of Congress and the President, the parties could not reach agreement on the bill's provisions, particularly those to reform the law's liability scheme. In September of last year, 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.[3] Both the Smith and Oxley bills included provisions embracing the "results-oriented approach" to Superfund cleanups advocated by AIChE. Much of the debate on the measures centered on the liability reform provisions of the bills, which would have granted some relief from the retroactive liability provisions of the Superfund law, but would not have provided the total repeal of retroactive liability that some in Congress desired. The major stumbling block to retroactive liability repeal was its cost. The Oxley bill was approved by a House subcommittee in November, but no further progress on the bills occurred.

Congress did, however, provide relief from Superfund liability for

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[2] See "Washington Environmental News" *Environmental Progress*, **15**, F7-F8 (Fall 1996).

[3] For a summary of these bills, see "Washington Environmental News" *Environmental Progress*, **15**, S7-S11 (Summer 1996).

lenders (P.L 104-208). The new law declares that lenders are not considered "owners and operators" (who are subject to Superfund liability) if they do not participate in the management of a vessel or facility.

The failure of the President and Congress to reach agreement on a budget late last year eliminated a source of funds for the Superfund program. The federal government's authority to collect the four taxes that finance the Superfund Trust Fund expired at the end of 1995. The budget reconciliation bill vetoed by the President in December 1995 would have extended the taxes on petroleum, hazardous chemicals, and imported substances made with hazardous chemicals until September 30, 1996, and the corporate environmental income tax would have been extended until the end of 1996.

Despite the failure of reform efforts and the expiration of the authority to collect the taxes that finance the Superfund Trust Fund, the program remains in operation with funding of $1.4 billion in fiscal year 1997.

TOXICS RELEASE INVENTORY

In response to two EPA proposals to expand the Toxics Release Inventory (TRI), Congress directed the General Accounting Office to conduct a detailed study of "community right-to-know" programs. The TRI, which is part of the Emergency Planning and Community Right-to-Know Act, requires certain manufacturing facilities to report annually on their releases to the environment of a mandated list of toxic chemicals. The list currently covers approximately 650 chemicals. In June of this year, EPA proposed to expand the TRI to require seven additional industries (metal mining; coal mining; electric utilities [coal and oil-fired generating facilities only]; commercial hazardous waste treatment; petroleum bulk terminals; chemical wholesalers; and solvent recovery services). In September, EPA declared its intent to draft a rule requiring facilities that report under TRI to include materials accounting information on their use of the listed chemicals.[4]

As part of the EPA appropriations bill for fiscal year 1997, Congress directed the General Accounting Office, which is an investigative arm of Congress, to study ways to improve the community right-to-know program to address community concerns about chemicals, evaluate EPA information-management practices, recommend methods to increase the accountability of federal agencies in complying with TRI, address the effectiveness at the local level of current community right-to-know mechanisms, and assess how existing and proposed community right-to-know programs support EPA's planning, budgeting, and accountability system.

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[4] AIChE's Government Relations Committee recently approved a policy statement related to this proposal. Copies of the statement, "Improving Measures of Pollution Prevention," are available from AIChE's Washington, DC, office. In addition, AIChE will be submitting comments to EPA on the chemical use information proposal.

ION EXCHANGE AND SOLVENT EXTRACTION, VOLUME 12

Jacob A. Marinksy and Yizhak Marcus, Marcel Dekker, Inc., New York, NY, (1995) 448 Pages, [ISBN No.: 0-8247-9382-X] U.S. List Price: $195.00

The twelfth volume of *Ion Exchange and Solvent Extraction*, like its predecessors, presents up-to-date information on emerging areas of ion-exchange technology, as well as in-depth discussion on selected aspects of ion-exchange theories. Nine chapters contributed by scientists and researchers from China, Germany, Israel, Japan and Russia are organized as follows: (1) high pressure ion-exchange separation of rare earths, (2) ion exchange in countercurrent columns, (3) recovery of valuable mineral components from sea water by ion-exchange and sorption methods, (4) investigation of intraparticle ion-exchange kinetics in selective systems, (5) equilibrium analysis of complexation in ion exchangers using spectroscopic and distribution methods, (6) ion-exchange kinetics in heterogeneous systems, (7) evaluation of the electrostatic effect of metal ion binding equilibria in negatively charged polyion systems, (8) ion-exchange equilibria of amino acids, and (9) ion-exchange selectivities of inorganic ion exchangers. These articles tend to reflect the current status and future trends of ion-exchange technologies for varied applications. In the book, a considerable emphasis is placed on exploring fundamental theories on ion-exchange equilibria and kinetics. References are provided at the end of each chapter.

Chapter 1 demonstrates the performance of high pressure ion-exchange chromatography (HPIEC) for separating rare earth elements. The chapter highlights the salient advantages of HPIEC over classical ion-exchange chromatography (CIEC). The chapter provides experimental data describing the quantitative relationship between the band migration rate and band length, the influence of the effluent concentration on the zone of the target ions, the length of overlap between neighboring zones, and the relationship between the composition of the two phases and the effluent concentration. Further, optimal operating parameters are proposed. The general field of rare earth elements separation by ion-exchange has been around for over fifty years now. However, the list of references for a chapter on such a general area appears to be quite short (only twelve).

Chapter 2 discusses ion-exchange in countercurrent columns for large-scale industrial applications. Main topics covered include theories on separation with flow reversal (inside the column, outside the column, and partial flow reversal in the column), separation of multicomponent mixtures, separation of mixtures by changing the interphase transfer directions, schematics of practical systems, and the dependence of the height of a transfer unit (HTU) on the phase motion rate. The chapter also provides a detailed comparison of the countercurrent and conventional fixed-bed configurations. It, however, failed to highlight the counter current system's shortcomings, which have held back its more frequent applications over the years.

Chapter 3 deals with ion exchange and sorption methods for recovery of valuable mineral components from sea water. Although the oceans in our planet are often the major sources of various minerals, viable recoveries are often impractical due to very low concentrations of the target solutes. This chapter provides a thorough review of existing and the underlying principles and proposes various process schemes for recovery of several macroelements (e.g. magnesium, potassium, and bromine) and microelements (e.g., lithium, uranium, rubidium, boron, strontium, molybdenum, vanadium, and other nonferrous microelements) from sea water.

Chapter 4 is devoted to intraparticle diffusion controlled ion-exchange systems, which are particularly applicable for selective ion-exchange systems. The authors' model is tested by fitting experimental kinetic data into the model simulated curves. This chapter also confirms the strong dependence of the intraparticle diffusion rate on diffusivity, selectivity factors, and bulk solution concentrations. The proposed model and related discussion offer an insight into various aspects of diffusion-controlled ion-exchange processes. However, the chapter is devoted solely to batch systems.

Chapter 5 introduces spectroscopic techniques as useful tools for analyses of ion-exchange equilibria. The chapter presents several applications of these approaches, including equilibrium analyses of strong complexation in anion-exchange phases, heterogeneous two-phase distribution analyses of complexation in ion exchanges, three-phase distribution in anion-exchangers, analyses of complexation at high loading in anion exchangers, analyses of complexation in chelating resins, and evaluation of stability constants of metal complexes. The spectroscopic technique discussed in this chapter may find useful applications in validating theoretical equilibrium models. However, the Donnan potential terms used in equations 9 and 10 are not in order.

Chapter 6 explores ion-exchange kinetics in heterogeneous systems for both batch and continuous flow-stirred reactors. By extending classical homogeneous film diffusion equations, this chapter examines the kinetic behavior of heterogeneous resin mixtures with respect to varying particle size, ion-exchange capacity, and separation factors. Some of the observations discussed with heterogeneous systems are counter-intuitive but often encountered in natural systems. Theoretical discussions presented in this chapter will advance understanding of some key natural phenomena.

Chapter 7 presents fundamental theory and experimental evidence for evaluating the electrostatic effect on metal-ion binding equilibria in negatively charged polyion systems, namely, carboxylate polyion systems, sulfate and sulfonate polyion systems, and phosphate polyion systems. Major aspects embrace acid dissociation equilibria of carboxymethyldextrans and their gel analogs, metal complexation equilibria of dextransulfates and sulfopropyldextrans gels, and Ca^{2+}-ion binding equilibria of heparin. The fundamentals of electrostatic interaction discussed in this chapter can be applied to polyelectrolytes, biological membranes, and synthetic macromolecules including polymeric ion exchangers.

Chapter 8 examines the ion-exchange equilibria and uptake mechanisms of amino acids by ion exchange. The speciation of amino acid is dependent on pH and ionic strength, and relative affinities of individual species towards ion exchangers are different. The chapter provides step-wise derivation of important equilibrium parameters, namely, effective distribution coefficients and average separation factors.

Chapter 9 is dedicated to inorganic exchangers and their selectivities toward cationic and anionic solutes. This chapter highlights several unique properties of inorganic ion exchangers in comparison with organic exchangers. Primary topics include the quantitative description of ion-exchange selectivity, acid strength of various inorganic ion exchangers (hydrous oxides, insoluble acid salts of polyvalent metals, and aluminosilicates), classification of acid strength, crystallinity effect, ion sieve effect, ion memory effect, and various types of ion-exchange isotherms.

On the whole, the collected papers in the book provide thorough discussions as well as current state of development in respective areas. However, the chapters seem to be disjointed to each other, i.e., the subject matters go from protein separation to diffusion-controlled kinetics to inorganic ion exchange. Chapters under a common binding theme would be preferred. In any event, every chapter stands on its own and the book will be found to be very useful to professional scientists and engineers involved in the area of ion exchange.

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GUIDELINES FOR WRITING EFFECTIVE OPERATING AND MAINTENANCE PROCEDURES

Center for Chemical Process Safety, American Institute of Chemical Engineers, New York, NY, (1996). 144 Pages, [ISBN No.: 0-8169-0658-0] U.S. List Price: $120.0

The U.S. Environmental Protection Agency (EPA) investigation of a 1994 chemical plant tragedy concluded that "...the explosion resulted from lack of written, safe operating procedures..." *Guidelines for Writing Effective Operating and Maintenance Procedures*, a new book from the American Institute of Chemical Engineers' (AIChE's) Center for Chemical Process Safety, specifically addresses overcoming this crucial shortfall. It was written by a team of experts in training, industrial chemical safety, and maintenance. The book explains how to write the operating and maintenance procedures essential for a properly trained staff and to meet applicable regulations for safe processes.

Operating and maintenance procedures have become an international issue. The U.S., Europe, and Canada have all issued or proposed regulations that require procedures for process safety purposes. The International Organization for Standardization (ISO) includes the control and use or procedures as a key element of a company's quality management system. These influences affect more companies each year, as they seek a global market for their products. Anyone who needs procedures to assure safe operations will benefit from this book. Operations and maintenance procedures are important in, but not limited to, the chemical and petrochemicals industries.

The introduction promotes the concept of viewing operating and maintenance procedures as vital plant components, such as a pump or reactor. Who would start up a new process without all of the pumps in place and tested? Accepting this idea, that procedures are components, and following the guidelines presented in this book, should produce a high quality procedure-management system. The second chapter examines several voluntary guidelines and regulatory requirements dealing with operating and maintenance procedures. The various guidelines, initiatives, and regulations reflect an emerging consensus that tie procedures to safety, environmental, and quality considerations. Understanding these requirements and recommendations will help assure that your procedures contain the critical information to run your process safely and effectively.

How to design an operating and maintenance procedure-management system and how to write the resulting operating and maintenance procedures are covered in Chapters 3 and 4. Six common steps are presented to determine tasks that require written procedures, along with six reasons why some procedure-management systems fail. The resources necessary to write the procedures are briefly discussed. The importance of utilizing human factors is stressed, along with the necessity of employee participation at all phases. The examples in the book clearly point out some common formatting errors found in many existing procedures manuals. The value of the T-format is clearly shown, along with effect of too much information being presented in a given space.

Chapter 5, devoted to defining the elements of effective procedures, contains a wealth of guidance that is clearly presented through extensive use of examples. All examples have a correct or good version along with an incorrect or bad version. Seeing the two together allows the reader to see how, all too often, poorly written procedures can be a hindrance rather than an aid to efficient operation and could lead to chemical release or injury. The necessity of clear and accurate titles, proper sequencing and identifying the end of a procedure are clearly illustrated. This is probably the most valuable chapter to anyone involved with defining, developing, rewriting, or reviewing existing procedures.

The writing of emergency operating procedures is covered in Chapter 6. Again, numerous examples are used to aid the reader in developing the appropriate procedures. Well-written emergency operating procedures can keep events from escalating by instructing the operators to perform critical actions, make effective decisions quickly, and focus attention on the emergency.

The basic requirements to access, review, approve, control, and maintain procedures is presented in Chapter 7. It also discusses the wide range of choices available in selecting the level of control and electronic document-control methods that may be of assistance. The key elements are assuring that procedures are updated, as required, using set rules, and that only current approved procedures are available to the users. A brief look at procedure development costs and benefits is presented in the final chapter.

Appendices A and B of the seven appendices list selected procedure initiatives, consensus codes, and regulations affecting procedures along with the common points among the API, OSHA, and EPA regulations. How to determine the tasks that require written procedures, procedure performance evaluation, and a procedure criteria checklist are given in the next three appendices. The last two contain numerous examples of formats for procedures and operating limits tables.

In summary, this book is recommended for anyone involved with defining, developing, rewriting, or reviewing operating and maintenance procedures. The importance and benefits of developing and implementing effective operating and maintenance procedures is thoroughly covered. I personally appreciated the extensive use of examples in Chapters 4, 5, and 6, along with the sample formats in the appendices.

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ENVIRONMENTAL CHEMODYNAMICS: MOVEMENT OF CHEMICALS IN AIR, WATER AND SOIL (2ND EDITION)

Louis J. Thibodeaux, John Wiley & Sons, Inc., New York, NY (1996) 593 Pages [ISBN No.: 0-471-61295-2] U.S. List Price: $69.95

The First Edition of Environmental Chemodynamics made an outstanding contribution to chemical engineers practicing in the burgeoning environmental arena. The First Edition addressed the important features of thermodynamics, especially applied to interfacial equilibria, intraphase transport processes (diffusion), and interphase exchanges in formulation and solution of environmental engineering problems. However, the participation of chemical engineers evolved rapidly in the decades of the 1980s and 1990s. The Second Edition of the book fails to reflect the explosion of knowledge in environmental engineering and science, and does not do justice to the contributions of the chemical engineering profession to this growth.

Chapter One includes a welcome statement of goals and objectives. The discussion of Units and Nomenclature is meticulous; it correctly points out the subtle problems of units and quantification, especially as related to "trace" constituents of environmental media. The entry-level chemical engineer may be more awed than educated; in short, the book serves as a function for formal teaching rather than self-guided instruction. The initial Example and the Problems are important teaching tools but rely too heavily on classic, overly simplistic models of in-stream assimilation and reaction processes. Teaching and References values would be enhanced by citation of recent approaches to stream quality analysis and regulation, e.g., health-oriented versus technology-oriented options for justification of industrial discharge limits.

Chapters Two and Three are nicely formulated approaches to the application of chemical engineering fundamentals to environmental problems. The Thermodynamics discussion is clear and concise. The deferential citation of Hougen et al. [page 36] is a mark of the author's great respect; it could be improved by additional references to other important works in applied thermodynamics, e.g., Denbigh, Putzer and Brewer, Sandler, etc. The early incorporation of data on seawater, soils, and rocks is outstanding; most chemical engineers, regardless of academic achievement, have little exposure to geology or soil science. The text creates an awareness of the role played by natural (prototypical) substances. The citation of Brady is excellent; the early chapters of Brady's book are suited to self-study on the physical and chemical characteristics of rocks and soils.

The reference to conditional equilibrium on page 58, relative to Figure 2.1-4, requires emphasis. It is all too often true that partition coefficients are site specific and cannot be transferred. A brief discussion of weathering, i.e., the kinetics of environmental aging, octanol/water partition relative to natural organic matter, and the extensive recent literature on solution mechanics (especially the work of Rao at the University of Florida) would illustrate this problem. The acronym "ATP" used on pages 78 and 79 will be misunderstood to mean Adenosine TriPhosphate by most biochemical engineers. The author does an outstanding job in Section 2.1K; Henry's Law is commonly misused, misunderstood, and misinterpreted by non-chemical engineers. Chapter Three continues the admirable bridge to the environmental from chemical engineering fundamentals; the References and Discussion establish a common ground, Bird et al., Danckwerts, Treybal, Schlicting, Stumm, etc., are time-proven sources of information and ideas.

Chapters Four and Five address air/water and water/solid interfaces. Both are instructive but rely too heavily on classic sources. The reader should be warned that this material is intended to integrate fundamentals with common receiving water management strategies. Practicing engineers engaged in water quality management activities must be aware of State/Federal regulatory attitudes and monitor/control methodology research. These chapters are not self-sufficient resources for water quality analysis and design.

Chapter Six is an excellent review of transport in the lower atmosphere and in the vadose zone in saturated systems. This material is essential and is foreign to most chemical engineers. As with previous chapters, reliance on historic sources of models and data renders the material presented insufficient for transport and remediation analyses; the reader must be aware of this situation. It is wise of the author not to attempt to incorporate recent developments in the text. Practitioners must consult the current literature. Books that attempt to provide guidance for practitioners tend to be short-lived. Material reprinted from Brady is generally good. Figure 6.3-3 is overly simplistic and the statement that the role of "bound" water is not significant is questionable; see page 401. Appendices A through E are well done; readers will find these appendices very useful.

In summary, this book provides a review of chemical engineering fundamentals within the context of geologic, atmospheric, and soil system processes that are generally unfamiliar to many of the author's students and colleagues. It is outstanding reading, in parallel with current literature, for environmental engineers. It will outlast other recent books that stress legislation, regulation, design, and monitoring practices too heavily, in lieu of fundamentals.

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ERRATUM

A review of *Hazardous Waste Management, 2nd edition*, written by Charles A. Wentz and published by McGraw-Hill Inc., appeared in our Fall issue [*Environmental Progress*, **15**, F11 (1996)]. The price of the book was incorrectly listed as $199. The actual list price is $69.

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Introduction to WWW. Environmental_Health_&_Safety.Com

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INTRODUCTION

Health and Safety of the workers and the general public is an important issue for environmental professionals working in the industry and governmental agencies. This is primarily due to the increase in use of chemicals, industrial accidents, governmental regulations, and public awareness of environmental problems. In order to make informed decisions environmental managers, engineers, and scientists need information from a variety of sources. The information superhighway can assist all of us.

In continuation of our efforts to accentuate the usefulness of the Internet as a repository of information and data [*1,2,3*], this paper focuses on the Environmental Health and Safety web sites on Internet. An in depth view of information pertaining to environmental health and safety which would be of immense help to environmental professionals as well as students seeking relevant material for their use is presented.

The world wide web (WWW) uses what are called Uniform Resource Locators (URL) to represent the hypertext links and links to network services within the HTML documents [1]. If one were to perform a word search on "Environmental Health and Safety" thousands of pertaining sites would pop up on the screen, which would entail hours of browsing to get the desired information. This paper provides a list of URLs, along with a brief description of each site containing information regarding Environmental Health and Safety, which would greatly reduce your search time.

INTERNET SITES FOR ENVIRONMENTAL HEALTH & SAFETY

Since a list of sites on Environmental Health and Safety is not easily available on the Internet we have made an attempt to create a comprehensive list of various sites available on the net. In addition to the URL's , the following is a brief summary of each of the sites:

• Agency for Toxic Substances and Disease Registry

http://atsdr1.atsdr.cdc.gov:8080/atsdrhome.html Links to the following resources can be obtained at this site.

1. HazDat, ATSDR's Hazardous Substance Release/Health Effects Database

http://atsdr1.atsdr.cdc.gov:8080/hazdat.html#A3.1

Hazdat is the scientific and administrative database developed to provide access to information on the release of hazardous substances from Superfund sites or from emergency events and on the effects of hazardous substances on the health of human populations [1].

2. ToxFAQs

http://atsdr1.atsdr.cdc.gov:8080/toxfaq. html

ToxFAQ's are short, easy-to-read summaries about hazardous substances that have been excerpted from the ATSDR Toxicological Profiles.

3. Public Health Statement Text Search

http://atsdr1.atsdr.cdc.gov:8080/query-phs. html

This search engine enables the World-Wide Web user to search for specific words or combination of words occurring in ATSDR's Public Health Statements. Taken from the Toxicological Profiles, the Public Health Statements offer easy-to-read summaries of many hazardous substances to which people might be exposed.

4. ATSDR/EPA Top 20 Hazardous Substances

http://atsdr1.atsdr.cdc.gov:8080/cxcx3.html

The priority list of hazardous substances prepared by ATSDR and EPA is provided out here. Each chemical is identified with a Rank Number and includes an ATSDR Public Health Statement.

5. Minimal Risk Levels (MRLs)for Hazardous Substances

http://atsdr1.atsdr.cdc.gov:8080/mrls.html

One can find the ATSDR Minimal Risk Levels (MRLs) for hazardous substances here.

6. Environmental Data Needed for Public Health Assessment

http://atsdr1.atsdr.cdc.gov:8080/ednpha.html

This site is a guidance manual published by ATSDR that describes the general purpose and focus of a public health assessment (PHA) and the data that is needed to produce a PHA.

7. Hazardous Substances & Public Health

http://atsdr1.atsdr.cdc.gov:8080/HEC/hsphhome.html

Hazardous Substances & Public Health is a quarterly newsletter published by the Agency for Toxic Substances and Disease Registry and can be found on-line at the above URL.

8. Software CLUSTER version 3.1

http://atsdr1.atsdr.cdc.gov:8080/HS/cluster.html

The CLUSTER (version 3.1) software download site is designed to help the researcher determine if there is a statistically significant chance that a cluster occurred other than by random phenomenon.

• DOE Office of Environmental Safety and Health, Home Page

http://nattie.eh.doe.gov/

DOE's Environment, Safety and Health (ES&H) Technical Information Services (TIS) is a collection of information services that provides safety and health professionals with reliable, accurate and current information to assist them in performing their jobs.

ES & H Info Center

http://nattie.eh.doe.gov:80/map.html

The ES&H InfoCenter provides multimedia access to Federal, industry and international information sources.

1. ES & H Documents and Publications

http://nattie.eh.doe.gov/docs/docs.html

DOE's Environment, Safety and Health (ES&H) Technical Information Services (TIS) is a collection of information services that provides safety and health professionals with reliable, accurate and current information to assist them in performing their jobs. The Environmental Safety & Health Documents and Publications provide links to the following sites:

a)ES&H Documents

http://nattie.eh.doe.gov/docs/documents.html

A selection of prominent documents generated by or of interest to professionals in the disciplines of environment, safety and health are included here. The various documents available at this URL include Environmental Health & Safety Plans, Occupational Safety and Health documents, The National Environmental Policy Act (NEPA) documents, Radiation Reports, site related Documents, U.S. Nuclear Regulatory Commission documents, and documents pertaining to Fire Protection Program, and Operating Experience Analysis and Feedback.

b) ES&H Publications

http://nattie.eh.doe.gov/docs/pubs.html

Bulletins, Newsletters, Hazard Alerts and other periodic publications containing time-sensitive data can be found at the above URL. ES&H InfoCenter Bulletin, ES&H Synergy, Safety and Health Bulletins, Safety and Health Notes, Safety and Health Actions, Safety and Health Hazard Alerts, Nuclear Reactor Safety, Health Watch, Operating Experience Weekly Summary, Office of Nuclear and Facility Safety (NFS) Safety Notices ES&H Updates, Safety and Health Connection, and Occupational Safety Observer can all be accessed from this web site.

c) Regulatory Information and Guidelines

http://nattie.eh.doe.gov/docs/regs.html

This page provides a collection of regulatory documents including the Environmental Guidelines, DOE Directives, DOE Orders & Standards, and other regulatory criteria and standards.

2. Information Services

http://nattie.eh.doe.gov/systems/services.html

Links are provided for ES&H InfoCenter, conferences and training information, medical links, special teams and tasks, and other information services. ES&H InfoCenter, provides multi-media access to Federal, industry and international information sources.

3. Database Services

http://nattie.eh.doe.gov:80/systems/datasys.html

The database services page contains primary ES&H databases, which include Comprehensive Epidemiologic Data Resource (CEDR), Human Radiation Experiments, Facility Profiles (FPIMS), National Environmental Policy Act (NEPA), Populations at Risk to Environmental Pollution (PAREP), Computerized Accident/Incident Reporting System (CAIRS), Accident Analysis Documents (MORT) Technical Research and Applications Center (TRAC), Occurrence Reporting and Processing System (ORPS), Occurrence Reporting and Processing System Graphical User Interface (ORPS GUI), Risk Information Management System (RIMS), Document Imaging System (DIS), Medical Surveillance Information System (MSIS), DOE Radiation Exposure Monitoring System (REMS).

• EPA Chemical Emergency Preparedness and Prevention Office

http://earth1.epa.gov:80/ceppo/

The EPA CEPPO home page contains profuse information regarding accident prevention and risk management planning, accident preparedness and right-to-know, emergency response, accident histories, and chemical information.

An exhaustive list of Fact sheets , legislation documents and extended links to Emergency Response and Chemical Information sites, are included in this site CEPPO has prepared the factsheets to summarize material in and related to legislation and regulation related to the program. Factsheets to be found on this page are those for clean air act and amendments related to chemical accident prevention and risk management, the emergency planning and community right-to-know act, and the chemicals. EPA chemical fact sheets provide summaries of information on over 300 chemicals including identifying characteristics, health hazards, ecological effects, and methods to reduce exposure to the chemical. The site also provides legislation and regulations pertaining to the clean air act and amendments related to chemical accident prevention and risk management, and the emergency planning and community right-to-know act.

• Occupational Safety and Health (OSHA)

http://www.osha.gov/

This OSHA home page provides information which can be used by health professionals, the academic community, lawyers, journalists, and personnel of other government entities.This page also includes links to publications, technical and other advisory information.

1. Publications

http://www.osha.gov/oshpubs

Information can be retrieved on topics related to employer's guide to teen worker safety, industrial hygiene, employee workplace rights, employer rights & responsibilities, federal employer rights & responsibilities following an OSHA inspection, personal protective equipment, guidelines for preventing workplace violence for health care and social, service workers, draft guidelines for workplace violence prevention programs for night, retail establishments, concepts and techniques for machine safeguarding, asbestos standard for general industry, fact sheets.

2. OSHA 's Priorities

http://www.osha.gov/oshinfo/priorities/

OSHA intends to address the issues emerging from its priority planning process through a combination of rule-making and other intervention tools. Summary sheets for individual priorities, listed below can be accessed at the above URL.

List of OSHA Priorities for which summary sheets can be located at the site are: Asphalt Fumes, Commercial Diving Safety, Crane and Hoist Safety, Diesel Exhaust, Hazardous Medications, Metalworking Fluids, Motor Vehicle Safety, Noise/Hearing Conservation, Occupational Asthma, Oil and Gas Well Drilling and Servicing, PELs Update (continuation of activity), Power Transmission and Distribution in Construction, Reproductive Hazards, Silica (Crystalline), Solvents, Synthetic Mineral Fibers, Welding, Cutting and Brazing, Workplace Violence. One can also read about the leading causes of occupational injury, illness and death.

3. OSHA Technical Information

http://198.17.175.40/OCIS/tech_info.html

The OSHA technical information page contains chemical sampling information for various chemicals listed by name and CAS number, list of approved blood lead laboratories in all the states, lead test kits, and fully validated OSHA analytical methods ready for downloading.

4.OSHA Standards

http://198.17.175.40/OCIS/standards_related.html

This site contains information pertaining to OSHA standards and related documents and includes draft of OSHA's proposed ergonomics protection standard, OSHA federal register, information collection requests, OSHA act of 1970 (amended 1990), OSHA's compliance assistance page, OSHA regulations, OSHA regulations, OSHA unified agenda, standards development, and standard interpretations.

5. Statistics & Data
http://www.osha.gov/oshstats/

The following information can be accessed through this web site:

SIC Manual provides the ability to search the alphabetic index of the 1987 version manual by keywords; access detailed information for a specified SIC, division, or major group; and browse through the manual structure.

Frequently Cited OSHA Standards is a query tool which allows the user to determine the most frequently cited Federal OSHA standards for a given SIC code. The SIC code may be determined by accessing the on-line SIC Manual.

Industry Profile for an OSHA Standard displays the industry SICs in which a specified Federal OSHA standard is most often cited. Information is shown at the SIC division and 2,3,4-digit SIC levels.

6.OSHA Software/Advisors
http://www.osha.gov/oshasoft/

The following software are available for download at the this site:

a) *The Asbestos Advisor 1.0* is interactive expert help. This software is for building owners, managers and lessees, as well as for contractors of building renovation, maintenance, and housekeeping services. Once installed on your PC, the advisor interviews you about a building. It then asks follow-up questions based on your answers, and writes a report on your responsibilities under the Asbestos rules.

b) *GOCAD* the Cadmium Standard Biological Monitoring Advisor, is interactive expert help. This software evaluates laboratory results (of required medical surveillance) under the Cadmium Standard. Once installed on your PC, it prompts for the necessary information and writes (required and optional) reports, letters, checklists, and statistics.

c) *The Permit Spaces Advisor (Public Test Version)* is a new expert system currently under development. It is interactive expert help for the Permit Required Confined Spaces Standard (29 CFR 1910.146).

• Centers for Disease Control and Prevention
http://www.cdc.gov/

1. Diseases, Health Risks, Prevention Guidelines and Strategies Information Page
http://www.cdc.gov/diseases/diseases.html

As the name suggests this site provides comprehensive information on prevention and cure of diseases, injuries and disabilities, health risks, specific populations, and prevention guidelines and strategies.

2. CDC Home Travel Information
http://www.cdc.gov/travel/travel2.htm

This page goes international. The site provides reference material for international travel, and health recommendations for different parts of the globe.

• National Institute for Occupational Safety & Health
http://www.cdc.gov/niosh/homepage.html

NIOSH is part of the Centers for Disease Control and Prevention (CDC) and is responsible for conducting research and making recommendations for the prevention of work-related illness and injuries. This page contains links to sites which deal with hazardous workplaces, disease prevention, worker protection and other environmental safety related information.

1. NIOSH Databases
http://www.cdc.gov/niosh/database.html

The National Institute for Occupational Safety and Health currently offers easy access to the databases such as IDLH Viewer, The National Agriculture Safety Database (NASD), NIOSHTIC, NIOSH Manual of Analytical Methods (NMAM), NIOSH Pocket Guide to Chemical Hazards (NPG), Registry of Toxic Effects of Chemical Substances (RTECS).

2. National Occupational Research Agenda
http://www.cdc.gov/niosh/nora.html

This site explicitly describes the National Occupational Research Agendae (NORA) Priority Research Areas, a few of which include disease and injury, work, environment and work force, research tools and approaches.

3. NIOSH Respirator Information
http://www.cdc.gov/niosh/respinfo.html

One can find a full text description and technical summary on respiratory protective devices certified under 42 CFR Part 84, at this site. In addition, the site also provides the NIOSH guide to the selection and use of particulate respirators, a current list of approved respirators, and respirator users' notices.

4. The NIOSH on-line Compendium of Occupational and Environmental Questionnaires
http://www.cdc.gov/niosh/compend.html

This is a collection of questionnaires relevant to the investigation of occupational or environmental diseases. At present the site contains a few questionnaires that focus on respiratory symptoms.

5. Health Hazard Evaluation Program
http://www.cdc.gov/niosh/hhe.html

This page contains NIOSH conducted field investigations of possible health hazards in the workplace, called Health Hazard Evaluations (HHEs), under the authority of the Occupational Safety and Health Act of 1970, which authorizes the Secretary of Health and Human Services, following a written request from employees, authorized representative of employees, or employers, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

With the help of user friendly instructions one can quickly learn what an HHE is, who can request an HHE, when to request an HHE, under what authority NIOSH conducts HHEs, how the results are reported, and more.

• American Industrial Hygiene Association
http://www.aiha.org/

This web site maintained by AIHA provides information on Industrial Hygiene and various articles pertaining to problems in the work environment. A synopsis of brochures can be for the following list of titles can be obtained at this site: Industrial Hygienists: Dedicated to Protecting People in the Workplace and the Community, An Ergonomics Approach to Avoiding Workplace Injury, Is Lead a Problem in My House?, Is Indoor Air Quality a Problem in My Home?, Do I Work in a Sick Building?, Career Works, and Career Works for Kids.

• Canadian Center for Occupational Health and Safety Server
http://www.ccohs.ca/

This site provides a comprehensive computerized information service on safe and healthy working environments called, CCINFO, delivered through compact disc

(CD\-ROM), an on-line system, CCINFO-line, and diskette products.

The Canadian Center for Occupational Health and Safety (CCOHS) promotes a safe and healthy working environment by providing information and advice about occupational health and safety. CCINFO assists thousands of users in some fifty countries in meeting their information needs.

- **EcoNet's Toxics, Hazards & Wastes Resources**

http://www.igc.apc.org/toxic/

This web site offers informational resource links, a few of which include:

1. Chemical Health & Safety Data
http://ntp-support.niehs.nih.gov/Main_pages/Chem-HS.HTML

Chemical Health & Safety Data, part of the Department of Health and Human Services' National Toxicology Program, allows search for chemical compounds by keyword and some excellent toxicology and physical/chemical data.

2. The Internet Consumer Recycling Guide
http://www.best.com/~dillon/recycle/

The Consumer Recycling Resources Guide provides a starting point for people with regular household quantities of material to recycle. Information is provided on toxic and hard-to-recycle materials, and a list of local recycling web pages in the USA.

3. The EXtension TOXicology NETwork (EXTOXNet)
http://ace.orst.edu/info/extoxnet/

The Extension Toxicology Network web page is maintained by the University of California, Davis, Oregon State University, Michigan State University, and Cornell University. The resources covered at this site include toxicology fact sheets, Pesticide Information Profiles (PIPs), and Toxicology Information Briefs (TIBs).

MSDS Information

With the help of the Internet it is now possible to obtain Material Safety Data Sheets on hundreds of materials [2]. The URL's of few of a sites which provide Material Safety Data Sheets on-line are:

1.gopher//gopher.chem.utah.edu:70/11/MSDS

This site which is maintained by The University of Utah contains a library of MSDS on hundreds of materials. This site is of excellent use to students and teachers for their learning and teaching purposes.

2. gopher://ecosys.drdr.virginia.edu:70/11/library/gen/toxics

This site is maintained by the University of Virginia and it supports a gopher server that contains a database of Chemical substance Fact sheets for various chemicals.

3. http://www.enviro-net.com/technical/msds

The enviro-net MSDS database is similar to the University of Utah database and it also includes a searchable index.

4. gopher://hazard.com:3000/7

This is a searchable Gopher index from Vermont SIRI, and uses the search function of your browser to search terms.

5.http://physchem.ox.ac.uk/MSDS

These Material Safety Data Sheets are provided by the Oxford University's Physical and Chemical Theoretical Laboratory and are gathered from a variety of net and other sources.

6. http://diamond.cicsr.ubc.ca.8080/wowf/web_msds_search-t?

The Material Safety Data Sheets are provided by the University of British Columbia.

- **Ergonomics**

Ergonomics means engineering the interaction between workers and their workplace . The focus of ergonomics is the consideration of humans in the design of man-made environments, objects, work procedures, etc., with the principal objective to increase the effectiveness of resulting man-machine systems, while maintaining human well-being.

1. http://www.virginia.edu/~enhealth/ERGONOMICS/toc.html

This link leads to educational hypermedia and information about defining and evaluating ergonomic risks, creating ergonomically appropriate workstations and preventing work-related musculoskeletal disorders (CTD's).

2. http://www.engr.unl.edu/ee/eeshop/rsi.html

As more and more educational work involves using computers, students and instructors alike need to be aware of the hazard of Repetitive Strain Injury (RSI) to the hands and arms resulting from the use of computer keyboards and mouse. The page provides a very brief introduction to RSI and includes book references and links to Internet resources.

3. http://www.cs.princeton.edu/~dwallach/tifaq/

This is the home page for the typing injury FAQ and typing injury archive The site contains general information about typing injuries, keyboard alternatives, alternative pointing devices, software monitoring tools, and furniture information.

4. http://www.lib.utexas.edu/Pubs/etf/#articles

This page is an attempt to gather and make available some of the more useful sources of ergonomics information that are available on the Internet. It is intended to supplement other documentation or programs that the General Libraries Ergonomics Task Force may produce or make available for library staff.

CONCLUSION

This paper can be used as a reference guide to environmental professionals. The information found in the sites listed in this paper range from fact sheets about toxic chemicals to publications about the latest in the field of environmental health and safety.

In addition web page URL's for a number of sites related to Ergonomics and Material Safety Data Sheets (MSDS) are also listed in the paper. A total of 51 web sites have been listed.

We recommend the sites maintained by OSHA and DOE Office of Environmental Safety and Health to be excellent sources of detailed and latest information in the field of environmental health and safety.

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Life Cycle Assessment Applied to Process Design: Environmental and Economic Analysis and Optimization of a Nitric Acid Plant

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Life Cycle Assessment (LCA) is an environmental auditing tool that quantifies the environmental burdens of an activity inclusive of all its related systems. In the past, LCA has been applied primarily to products, but recent literature suggests it also has potential as an analysis and design tool for processes and services. This potential arises from the unique ability of LCA to link the environmental burdens of a process with its mass and energy flows. The aim of this work is to apply LCA as a tool for process design rather than one for product assessment. A nitric acid plant formed the basis for a case study wherein LCA was used to quantify and compare environmental performance of a number of design alternatives aimed at waste reduction. Economic models for the alternatives were formulated and linked to the environmental models to perform a multiobjective optimization with the express aim to maximize economic returns and minimize environmental impact. The comparative study showed that one design alternative was clearly superior from an environmental point of view. The optimization demonstrated that operational changes could result in significant environmental improvement at minimal economic cost. Future work in this area should focus on the allocation of environmental burdens from multiple-output processes as well as extending the analysis to include environmental and economic impacts of all related downstream processes.

INTRODUCTION

Life Cycle Assessment (LCA) is gaining wide acceptance as a method for estimating the environmental impacts associated with a given product, process or activity [*1*]. LCA has been described as "a process to evaluate environmental burdens by identifying and quantifying energy and materials used and wastes released to the environment; and to identify and evaluate opportunities to effect environmental improvements. The assessment includes the entire life cycle of the product, process or activity, encompassing extracting and processing raw materials; manufacturing, transportation and distribution; use, re-use, maintenance; recycling, and final disposal" [*2*]. Most of the LCA literature assumes a product-centered approach [*3, 4, 5, 6, 7, 8*], but recent articles also suggest the unexplored potential of LCA for the design of processes [*9, 10, 11*]. From the viewpoint of a chemical engineer, these two independent goals converge into one, as the engineer's 'product' is in fact the process which must be designed and operated. This work focuses on the application of LCA as a system analysis and decision-making tool for managers and engineers.

The problem facing decision-makers is how to accommodate both economic and environmental constraints in the design and operation of processes. Past attempts based on economics centre around cost-benefit analysis [*12*]. These approaches attempt to 'trade off' environmental and economic assets with an aim to maximize differences between socio-economic benefits of an activity against the financial and environmental liabilities. Such practices ultimately seek to attach a monetary value to the environment, and are therefore fraught with difficulty [*13*].

Alternatively, tools such as Environmental Impact Assessment and Risk Assessment attempt to address the problem from an environmental point of view, and treat economic considerations as secondary. These two methods are unsatisfactory for a number of reasons. Firstly, they tend to limit their discussion of environmental effects to those occurring with a small, site-specific region [*14*]. Secondly, they focus on process inputs and outputs rather than the process itself, and thus fail to offer suggestions for improving the process as a means to reducing waste. As a result, the economic consequences of such assessments tend to be driven by legislative constraints and are thus strictly punitive. A more process-specific methodology is a waste minimization strategy, which may have benefits both environmentally and economically through reduced waste and cost of waste treatment and by increased process efficiencies [*15*]. The downfall of this methodology is its lack of consideration for the long-term, far-reaching or cumulative environmental impacts of output streams.

Life Cycle Assessment may prove to overcome these problems and therefore establish a link between the environmental impacts, operation and economics of a process. LCA offers an expanded environmental perspective, considering impacts from resource extraction through to end product use and disposal. At the same time, LCA relates these effects to the mass and energy flows into, out of and (we claim) within a process. Thus, LCA has the ability to be both process specific and environmentally broad-based.

Within this context, the aims of this present study were:

1) to use LCA as a means to quantify and compare the environmental performance of a number of alternative process designs for a given system.
2) to undertake an assessment of the economic performance of the selected system.
3) to use the economic and environmental performance of a system as a basis for a multiobjective optimization whereby economic returns are maximized and environmental impacts minimized.

Nitric acid production was chosen to demonstrate this approach. Desirable features of the nitric acid system were its *simplicity* (few material and energy flows with well known technologies; one principal waste and product stream), *suitability* (offering opportunities for process improvement or modification), *significance* (in relation to other industrial processes) and *availability of data* (relating to economics as well as mass and energy information).

Two variations on the basic process design were chosen —one, a common 'end of pipe' solution to gaseous emissions, the other following waste minimization principles. The mass and energy balances of the process and its design alternatives were verified by computer simulation. This information was then used as the basis for establishing potential environmental impacts using LCA methodology. Economic models were constructed using projected cash flows and rates of return. The environmental and economic models were used as the basis for a multiobjective optimization, building upon the methods of Ciric and Jia [*16*] and Clark and Westerbrug [*17*]. These techniques iteratively calculate a Pareto-optimal or 'trade-off' curve by optimizing linear combinations of the objective functions.

This paper outlines the results of this study and highlights both the potential for LCA as a design tool and some issues that remain to be addressed in future work.

DESCRIPTION OF CASE STUDY

A low pressure nitric acid plant using Uhde technology was selected in co-operation with a local manufacturer of agricultural fertilizers. The process operates at 3.25 bar gauge (barg) producing roughly 30000 kg of 56% nitric acid per hour. A significant effluent from this process is a 'tail' gas stream containing 107 kg/h of nitrogen oxides (NO_X). A simplified schematic diagram of the process is shown in Figure 1. Note that compression (1) consumes both electrical energy and that which is derived from tail gas (4) and steam turbines (5).

One proposed variation on the basic design was addition to the tail gas stream of a selective catalytic reduction (SCR) unit to reduce NO_X levels. Data from the operating company indicate that NO_x emissions would be reduced from 107 kg/h (1432 parts per million) to 7.3 kg/h (100 ppm). The SCR consumes an additional 56.6 kg/h of ammonia as a reducing agent and requires a marginal increase in process heating requirements to raise tail gas temperatures for effective operation.

The second design option consisted of a pressure increase within the absorption system (3 in Figure 1) to 7.5 barg. Increased pressure would improve the efficiency of NO_x absorption, thus simultaneously increasing nitric acid output and decreasing gaseous effluent. Literature indicates an expected NO_x output level of 230 ppm with this revised configuration [*18*].

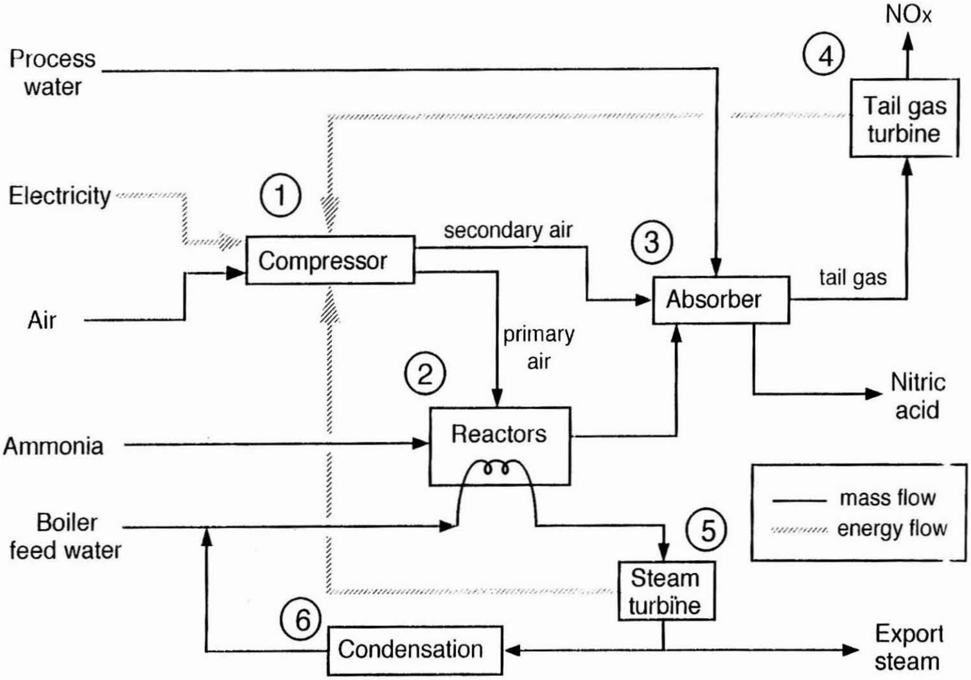

FIGURE 1 Process schematic for a nitric acid plant.

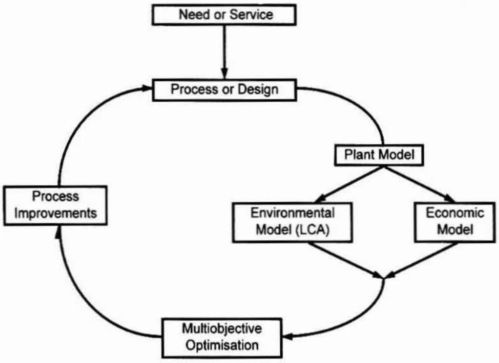

FIGURE 2 General improvement methodology for processes.

DEVELOPMENT OF MODELS

To quantify analysis of the different design alternatives, it was necessary to construct models of both the environmental burdens and the economic performance of each option. The models were dependent upon mass and energy flows throughout the process and therefore plant modeling and validation of these mass and energy flows was required. Following from this, LCA was used to quantify the environmental performance, while local cost data formed the basis of the economic model. These two models were used in concert to perform the overall process optimization.

The proposed relationships between these models is shown in Figure 2.

The existing process or design forms the basis for a plant model. The material and energy flows and the economic parameters of this model are then used to develop environmental and economic models, respectively. These latter two models form the basis for a multiobjective optimization, the results of which can be used to help identify potential improvements to the original process. The proposed methodology is thus iterative in nature, and limited only by the sensitivity of models to parameters of interest within the process design.

MODEL ASSUMPTIONS AND VERIFICATION OF FLOWS

As the economic and environmental models were both highly dependent upon mass and energy flows in the system, an essential preliminary step was the verification of the mass and energy balances throughout the process.

Material and energy flow information provided by the operating company was used to validate a detailed process flowsheet produced on HYSIM™ —a rigorous process simulator.* Some of the simplifying assumptions made were:

1. the platinum-rhodium catalyst lost from the reactor formed an insignificant environmental burden and was ignored.
2. the modeling of complex reaction pathways relating to absorber performance used only NO and NO_2.
3. the cooling water system was excluded from the simulation. Cooling water is a separate loop within the process and did not significantly affect the values of the energy and mass flows in the synthesis steps.

Similar mass and energy simulations were constructed for each of the design alternatives.

Development of Environmental Models using LCA

The recent literature contains extensive coverage of LCA methodology [*4, 5, 6, 7, 8, 19, 20*]. Despite lack of agreement over the details of this methodology, the overall structure has been established. Initially, a *system definition* specifies the basis of the calculations and all processes to be included in the analysis. Mass and energy flows within the system are quantified during the *inventory analysis*, followed by the *impact assessment* phase where these flows are linked to environmental problems by comparing them with the environmental 'burdens' associated with specific quantities of reference materials. Finally, the *improvement assessment* phase focuses on changes to the system to improve its overall environmental performance.

LCA is a very data-intensive procedure and computers are essential tools in the inventory analysis and impact assessment phases. For this study, the Excel-based software PEMS was used.** This software permits the creation of functional 'modules' which act as the building blocks for the model of the process under consideration and which are linked by material and energy flows specified by the user. These modules may be defined as general functions (e.g., transport of raw materials to the process) or as specific operations (e.g., compressors, as shown in Figure 1). The mass and energy streams into and out of the process, as well as those linking each module, form the basis for the impact assessment.

In this study, a basis of 30000 kg/h of 56% nitric acid was chosen. This corresponds to the hourly output of the existing production facilities. Furthermore, environmental burdens of 'upstream' processes such as ammonia and electricity generation were included in the study, but downstream processes using nitric acid were not. The study was therefore 'cradle-to-gate', rather than the more comprehensive 'cradle-to-grave' analysis. There was no loss of significance in limiting the analysis to the production stage, since it was envisaged that all product use steps would contribute equally to downstream impacts regardless of the production method.

In the inventory analysis phase, individual unit operations and their corresponding mass and energy streams from the HYSIM™ plant models were consolidated into functional modules appropriate for use by PEMS. These functional elements were similar to those shown in Figure 1. Pre-defined modules for ammonia production and electricity generation from the PEMS database were also included. Unlike the cooling water system which was ignored, the boiler feed water and steam generation loop (2, 5 and 6 in Figure 1) was included in the environmental models because steam is exported from the process and thus forms an energy 'credit'.

The impact assessment calculation is performed within PEMS by comparing constituents of each input and output

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**By Hyprotech International, #400, 119-14th St. N. W., Calgary, Alberta, Canada, T2N 1Z6.*

*** Version 2.0, PIRA International, Randalls Road, Leatherhead, Surrey, United Kingdom, KT22 7RU.*

stream against standard quantities of a set of reference components. The measured environmental burdens of each constituent relative to these reference components are stored in a matrix known as a 'template', which takes into account that each constituent may contribute to more than one type of recognized environmental problem (e.g., greenhouse effect, ozone depletion, acidification). After scaling the environmental burdens due to each constituent on the basis of relative quantities and template values, the contributions towards each type of environmental problem are summed to produce an 'effect score'. In our case we have retained, as a unit of measure, an effect score which is normalized as a percentage of world burden figures. For a given process, the set of all such effect scores corresponding to specific environmental problems forms the 'environmental profile' for the process.

The impact assessment methodology outlined above is a 'problem oriented' approach. PEMS also offers the choice of a 'medium oriented' or as it is often called, the 'critical volumes' approach. Instead of summing contributions to individual environmental problems, this approach calculates the volumes of clean air and water needed to dilute the constituents in output streams to existing legislative limits, and landfill volumes required for solid waste deposits. In this study, we chose the 'problem oriented' approach because of the clear links of input and output streams to well known environmental problems. For example, the tail gas stream consisted of NO_x and air. The environmental problems associated with NO_x are well known (i.e., acidification, greenhouse effect, photochemical smog) and so clear relationships between mass flow in the tail gas stream and effect scores for these problems were expected.

At issue, is the task of ranking the effect scores corresponding to different environmental burdens in terms of their relative environmental significance. Most commonly, this exercise requires some subjective judgment of critical impacts based on a host of non-technical factors. In our assessment, we chose to sidestep this issue in the following way: a linear weighting and summation procedure was used to calculate aggregate 'environmental index' scores [4] for each design option. Following on from Azapagic and Clift [21], the weighting factors of environmental 'significance' were based on the marginal changes in each effect score due to a marginal change in mass of product output from the process. In effect, this says that there is no *'a priori'* ranking of environmental impacts, but rather that significance is determined solely on the basis of a differential mass allocation. Whilst the "universality" of this approach is open to debate, it should be recognized that the primary objective of this exercise was to produce an environmental assessment of alternative process designs which could be rated along with suitable economic performance indicators, which, themselves, are commonly identified through marginal changes in materials and energy throughout. HYSIM^{TM} was used to recalculate mass and energy flows throughout the process due to a 100 kg/h increase in the production of nitric acid and the resulting flows used to form the basis of another LCA. The percentage difference in effect scores between the original and augmented case were then divided by the percentage increase in mass flow to calculate the weighting factors. For each design, effect scores were multiplied by the weighting factors and the products summed to produce the 'environmental index'.

TABLE 1. Values used in Economic Model

Parameter	description	Value
Capital cost	- Original plant*	82.2×10^6
	- SCR modification	6.0×10^6
	- High pressure modification	16.5×10^6
Annual operating cost	- Original plant	8.0×10^6
	- with SCR unit installed	11.6×10^6
Tax rate (%)		50
Inflation rate (%)		10
Lifetime of plant (years)		30
Selling price	- nitric acid	165
Purchase price	- ammonia	470
	- electricity (per k Wh)	0.11
	- steam (per 1000 kg)	30
	- water (per 1000 kg)	1.4

*All prices in 1994 South African Rands 1$U.S. = 3.65 R.

Development of Economic Models

The existing nitric acid plant was constructed in 1967. Capital costs provided by the operator were extrapolated using the Marshall and Swift indices and converted to 1994 equivalents. Operating costs, commodity prices and capital costs of the two proposed design modifications were obtained from the operator or estimated from standard reference texts [22, 23].

Values for economic parameters are shown in Table 1. An Excel spreadsheet was used to calculate projected cash flows and discounted rates of return over the plant life as well as the annual rate of return.

Formulation of the Multiobjective Optimization

Environmental and economic models for the existing plant design were chosen as the basis for the optimization because their corresponding mass and energy flows and economic information were more reliable than for the other design alternatives. Pressure in the absorption columns (P) was chosen as a 'decision variable' because of the sensitivity of tail gas NO_x levels to this parameter. In general, the choice of decision variables needs to be addressed through a process design methodology, the details of which are beyond the scope of this paper.

The first step in the optimization routine was the construction of equations linking P to the mass and energy flows throughout the process. As the mass and energy flows determined both the environmental profile (via the LCA) and the economic returns (via prices of inputs and outputs), linking column pressure to mass and energy effectively made the environmental and economic profiles dependent functions of the single independent variable P.

To develop these relationships, mass balance equations were constructed over the absorption process with the absorption efficiency (e) an unknown parameter. The mass flows of NO_x, nitric acid, water, oxygen and nitrogen were then determined as functions of 'e'. One of the resulting expressions, that for NO_x in the tail gas stream, was equated to an empirical relationship between the output NO_x level and the absorber pressure as provided by the operating company. The resulting expression related absorption efficiency to P and was used to determine the mass flows of the other materials in terms of P. Column pressure also affected the energy balance via the compression duty. For simplicity, it was assumed that all changes in energy requirements were satisfied by variations in electrical input. A correlation from the literature was used for the relationship between compression work and pressure [*24*].

The relationships between column pressure, electrical compression work and absorption efficiency were used to convert the economic and environmental models to functions of P. These revised models formed the objective functions for the optimization. The problem was to maximize the economic return (E) and simultaneously minimize the environmental index (M) of the process for column pressures over their normal operating range.

The method of Ciric and Jia [*25*] was used to find the resulting Pareto-optimal or 'trade-off' curve. First, the endpoints of this curve were located by maximizing each objective independent of the other within the constraints of column pressure. A number of interior points were then found via an iterative procedure whereby the linear combination E-aM was maximized for different values of a, defined as the slope of the line joining the endpoints of a segment of the trade-off curve. Optimum values of the function for each different value were found using the 'Solver' function in Excel.

RESULTS AND DISCUSSION

Comparison of Environmental Performance

The normalized effect scores for each design option are presented in Figure 3. The values in these 'environmental profiles' are derived during the impact assessment procedure by normalizing the calculated effect scores for each alternative design against the world annual effect scores obtained from the databases of PEMS. This provides for more meaningful comparisons among specific but unrelated environmental problems, as well as a framework from which to compare alternative designs with different configurations and mass flows.

From Figure 3, it can be seen that for all designs, the environmental burdens associated with acidification are relatively high due to nitric acid in the product stream (downstream impacts considered) and NO_x in the tail gas stream. The high values of fossil reserve depletion arise from two contributions, since extraction of hydrocarbons used to produce ammonia and coal required for electricity generation are both accredited to the nitric acid process. This reflects the ability of LCA to encompass 'cradle' activities within the environmental profile of an activity.

The high pressure modification is clearly superior to any other alternative, as all its effect scores are less than, or at least the same as, their counterparts for the original design or SCR case. The SCR modification provides an improvement in all environmental burdens save for depletion of fossil reserves and ozone, which are exacerbated upon operation of the SCR. This anomaly results from the additional ammonia consumed by the unit, and highlights a difficulty in comparing environmental performance of different processes on the basis of a set of effect scores. Without some form of relative valuation for each environmental problem, it is unclear how to rank the environmental desirability of the original design and the SCR alternative.

Favoring the SCR unit implies an equal importance amongst all environmental burdens, an assumption that may not be valid in practice. Note that in this instance, the LCA model provides useful information for decision-makers, but is not prescriptive. Instead, it makes explicit the 'trade-offs' between problems and thus clarifies the basis for future decisions.

Economic vs. Environmental Performance

The environmental index and annual rate of return for each design option are shown in Figure 4. The SCR plant has the lowest rate of return because the capital cost of the unit provides no additional revenue, whereas the high pressure modification increases efficiency of absorption and therefore increases production rates. As anticipated from the environmental profiles, the high pressure process has the lowest index value and therefore is most environmentally desirable.

These results demonstrate the potential benefits of a waste minimization approach over 'end of pipe' solutions to a problematic waste stream. The high pressure plant attempts to reduce the waste NO_x at its source, and in so doing provides both an environmental benefit and a payback

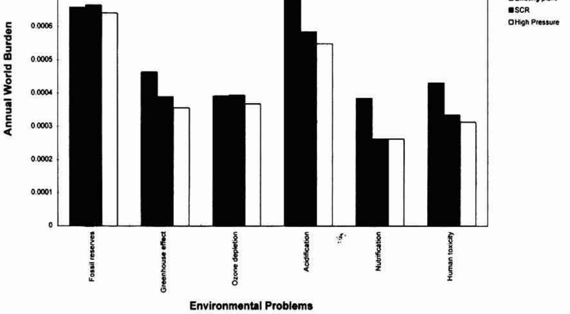

FIGURE 3 Environmental profiles. Normalized effect scores for three design alternatives.

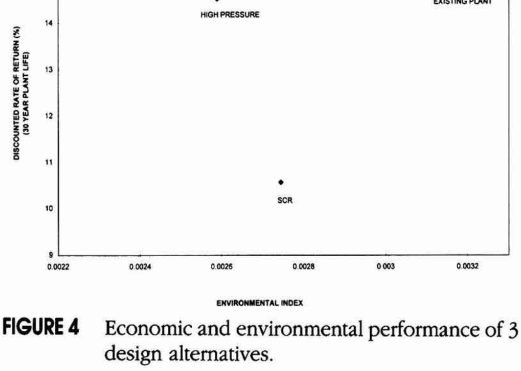

FIGURE 4 Economic and environmental performance of 3 design alternatives.

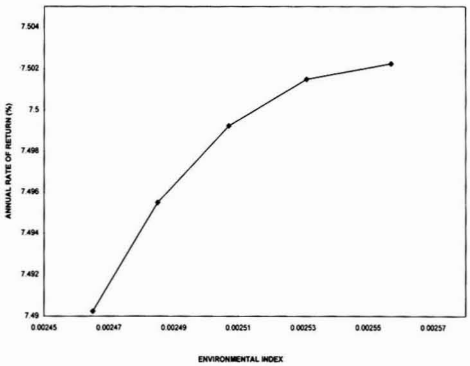

FIGURE 5 Trade off curve: a multiobjective optimization of existing plant.

on capital investment through increased process efficiency. The SCR unit, however, provides only a financial liability.

Multiobjective Optimization

The optimization problem outlined in this study entailed the simultaneous maximizing of economic returns and minimizing of environmental impact, subject to constraints on the absorption column pressure. In general, the objectives are conflicting and therefore a unique optimal solution is improbable. Instead, a number of sub-optimal solutions are likely, wherein one objective benefits to the detriment of the other albeit in the best possible way. The locus of all such points forms the solution set for the problem, and is known as the 'trade off' curve. The trade off curve for this problem is shown in Figure 5.

The end points of the trade off curve are obtained when each objective is optimized without regard for the other. The environmental index reaches a minimum when pressure is maximum because recovery of NO_x is maximized. The maximum economic return occurs at an intermediate pressure, where recovery of NO_x is relatively high, but compression costs are relatively low.

The points in the locus represent the best way to satisfy both objectives, but do not suggest which operating point should be chosen. Therefore, as with the environmental profiles, the curve is an aid to decision making but is not prescriptive. In this case, the curve flattens in its upper regions, suggesting that a slight increase in operating pressure would cause little economic sacrifice but substantial environmental benefit. This is a valuable conclusion in that it quantifies the gains and losses and therefore goes beyond the qualitative realm which until now has been the only means of analysis available.

FUTURE DIRECTIONS

This case study was carefully selected for its simplicity and utility as an investigative device. Results should therefore be taken as demonstrative rather than definitive. To enhance the value of such a methodology as a system analysis tool, it must be generalized and made robust. This means that any process or design at any level of complexity should, in principle, avail itself of the method. To that end, a number of obstacles need to be overcome. These can be loosely categorized either as being due to limitations in system modeling, related to unresolved issues in LCA methodology, or associated with optimization techniques.

Process and System Modeling Issues

A general methodology needs to accommodate both batch and continuous processes, those with internal and external recycle streams and systems with multiple input and output streams. Furthermore, since the 'product' in question is in fact the system under consideration, and since an input to this 'product' typically includes plant equipment and structures, the environmental burdens associated with equipment manufacture and process construction need to be considered. This goes against current LCA conventions, and requires entirely new areas of study. Finally, comprehensive methodologies must include environmental burdens of downstream processes and ultimately accommodate systems of a regional, national or even global scale.

Issues Related to LCA Methodology

The most significant problem constraining design-oriented applications of LCA is lack of agreement over allocation of environmental burdens to multiple input and output streams. This prevents adequate downstream modeling of related systems and thus reduces the legitimacy of the technique [*21*].

A second problem relates to the subjective nature of the valuation and weighting procedures wherein environmental problems are ranked in relative importance. In this study, an impartial method has been used to calculate weighting factors based on response of the environmental model to changes in process variables. A drawback of this method is the failure to include sociological aspects into the valuation. Perhaps these may be accommodated via a modification of the current method thus. If the 'medium-oriented' or 'critical volumes' approach is used as a basis for the environmental model in favor of the 'problem-oriented' approach adopted here, then sociological factors would be implicitly included via the legislative constraints that form the basis for the control volume approach.

Issues Related to Optimization Techniques

In this study, construction of objective functions was explicitly dependent on an empirical relationship between absorber performance and plant operating variables. In principle, empirical relationships are unnecessary, and development from rigorous engineering design and performance calculations is possible. This implies that the model and optimization methodology applied here to a case study is applicable not only to existing processes, but also to projects at the design feasibility phase.

In order for the optimization methodology to be generalized, multiple decision variables of both a continuous and discrete nature must be accommodated. This will permit optimization not only of process operation, but also of equipment selection and location. The process modeling for such cases promises to be complex, and newly developed techniques such as mixed integer non-linear programming may be required. Ciric and Jia [*16*] also mention extensions to their techniques applicable to discrete variables which may be useful in optimizing the choice of process technology.

A further extension to the optimization methodology may be the use of three or more objectives, particularly as a means to avoid the valuation step. Instead of valuation and consolidation of effect scores into a single environmental index, perhaps optimization can be based on minimization of *each independent effect score* in addition to the economic objectives. Once again, modeling and solution of such problems may prove to be difficult.

CONCLUDING REMARKS

It may be argued that some results of this study were intuitively obvious, thus calling into question the need for such an elaborate analytical procedure. However, we point out that this consistency with intuitive judgements should be taken as confirmation of the validity of the techniques, and thus suggest its suitability for problems where the relationships are perhaps not as straightforward.

In summary, the proposed methodology is initiated with an existing process or design which forms the basis for a plant model. The material and energy flows and the economic parameters of this model are then used to develop environmental and economic models, respectively. These latter two models form the basis for a multiobjective optimization. The environmental model identifies which areas in the process should be considered for the optimization. The important operating variables in these areas are chosen as the decision variables for the optimization, then the objective functions are formulated by expressing the models as functions of these decision variables. Finally, a method such as that of Ciric and Jia [*16*], is used to find solutions to the multiobjective optimization problem, and these solutions then inform the original process regarding potential improvements.

The significance of this work arises not from the numerical values derived, but from the possible ramifications of the methodology. It has been shown that LCA can quantify environmental performance of a process. This feature has been used to both compare environmental performance of design alternatives and to establish an objective link to economic performance via the mass and energy flows in the process. Results of the comparative study emphasized the potential advantages of waste minimization techniques over typical 'end-of-pipe' solutions to effluent problems. The links provided by LCA were exploited to optimize both the environmental and financial performance and thus provide a potentially powerful decision making tool. A more objective means of valuation and derivation of weighting factors were described and applied. Finally, suggestions have been put forward as to possible extensions of the techniques herein.

ACKNOWLEDGMENTS

The co-operation of the management and staff of Kynoch Fertilizer Ltd. is gratefully acknowledged.

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Air Emissions of Volatile Liquids Spilled on Sands

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Simple laboratory experiments simulating a spill of a volatile liquid on sands were conducted. Hexane was spilled onto both initially dry sand and water-wetted sand at near field capacity. The experimental conditions approximated the assumptions of a theory developed by Thibodeaux (1979). Predictions of a modification of this model were generally in good agreement at early times with data on the rate of volatilization. The modified model can be used to estimate air emissions of a volatile liquid spilled on sands.

INTRODUCTION

Gasoline and solvents spilled onto soils are a potential source of both groundwater contamination and air emissions. Such liquids infiltrate into the soil and travel downward in the unsaturated zone due to gravity. A fraction of the nonaqueous-phase liquid is trapped by capillary forces in the pores of the unsaturated zone. This liquid, retained within the unsaturated zone, may be a long-lasting source of atmospheric contamination. Gasoline and many common solvents have sufficiently high vapor pressures at soil temperatures to evaporate and diffuse to the surface resulting in air emissions.

Many numerical models [*1*, *2*] have been developed to predict the volatilization of liquid in the unsaturated zone. Thibodeaux [*3*] developed a very simple model describing the evaporation and diffusion of a volatile liquid spilled onto soils. A simplifying assumption of this approach is the instantaneous and uniform contamination of the soil due to the spill. Competing processes such as sorption of the liquid or its vapors to soils, chemical and biochemical reactions, and solubilization are ignored. The soil is assumed to be dry, isothermal, and of constant porosity. Thibodeaux and Hwang [*4*] extended this model for use in estimating the air emissions from landfarming of petroleum wastes. Dupont [*5*] compared predictions of the latter model with data from a laboratory experiment simulating landfarming of hazardous wastes. The data had a slope similar to that of the theoretical predictions, but the emission rates were a factor of 2 to 10 less than predictions. Wetherold and Balfour [*6*] compared data from a laboratory simulation of landfarming of hazardous waste to predictions of this theory.

This paper presents volatilization data from a simple laboratory experiment that simulated spills of a volatile liquid on sands. Experiments were conducted on both initially dry sand and water-wetted sand at near field capacity. The experimental conditions approximated the assumptions of Thibodeaux's original theory. The measurements are compared to the predictions of this model.

THEORY

Fick's Law governs molecular diffusion of a gas within porous media:

$$J = -D_e \frac{dC}{dz}, \tag{1}$$

in which J is the flux, C is the concentration, D_e is the effective molecular diffusion coefficient of the gas in the porous media, and z is distance perpendicular to the flux. Due to the tortuous path and restricted cross-sectional area for diffusion, the effective diffusion coefficient is less than that of the gas through air. The effective diffusion coefficient is frequently expressed by the following relationship:

$$D_e = \frac{D_0}{\tau} n, \tag{2}$$

in which D_0 is the molecular diffusion coefficient of the gas in air, n is the air-filled porosity of the sand, and τ is the tortuosity of the medium. A simple model for the effective diffusion coefficient was given by Millington [*7*]:

$$D_e = D_0 n^{4/3}. \tag{3}$$

Given a measurement of tortuosity τ_1 at air-filled porosity n_1, Equation 3 can be used to correct the tortuosity empirically for changes in the air-filled porosity due to the presence of water and other liquids:

$$\tau(n_2) = \tau(n_1)\left(\frac{n_2}{n_1}\right)^{1/3}. \tag{4}$$

Thibodeaux [*3*] presented a simple, idealized model for the evaporation and diffusion of a volatile liquid from a

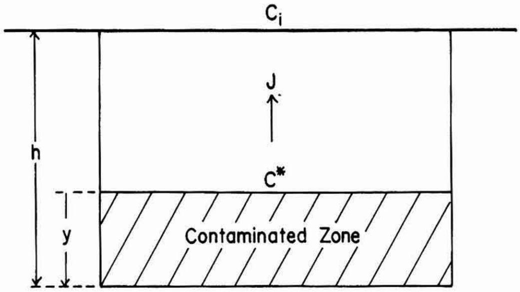

FIGURE 1 A cross section of contaminated porous medium.

porous medium such as may occur due to a spill onto soils. The initial concentration of the liquid within the porous medium is assumed to be uniform from the surface of the medium to a depth h as shown in Figure 1. At $t = 0$, the liquid is allowed to evaporate and diffuse to the surface. The medium and liquid are assumed to be isothermal. As the volatile liquid evaporates and its vapor diffuses to the surface, a "dried out" layer forms. Evaporation occurs at the interface between this dried out layer and a layer with uniform concentration of the volatile liquid. The thickness of the contaminant layer is y, and the thickness of dried out layer is $(h - y)$. The diffusion process is modeled as quasi-steady-state, one-dimensional diffusion across a layer of thickness $(h - y)$. The mass concentration of vapor at the bottom of this layer is C^* corresponding to its equilibrium vapor pressure with respect to a plane surface. The vapor concentration at the top of this layer is C_i. With these assumptions, the mass flux of vapor is

$$J = \frac{D_e}{(h - y)} (C^* - C_i). \tag{5}$$

If the mass of liquid spilled is M and the cross-sectional area of the spill is A, the change of depth of the evaporating front with time is given by

$$-(h - y)\,dy = D_e \frac{hA}{M} (C^* - C_i)\,dt. \tag{6}$$

This can be integrated to give an expression for $(h - y)$:

$$(h - y) = \left[\frac{2 D_e A (C^* - C_i) h t}{M}\right]^{1/2}. \tag{7}$$

This model ignores sorption of liquid and vapor, chemical and biochemical reactions, and changes of the equilibrium vapor pressure with the curvature of the volatile liquid's interface.

EXPERIMENTAL METHODS

Simple Stefan tube experiments were conducted to estimate the diffusion coefficient of hexane in air [8]. The tubes were 15 mm diameter glass tubes that were 150 mm long.

Bulk sand with a composition of 99.1% sand, 0.8% clay, and 0.1% silt was sieved. A coarse fraction, 1.0 to 2.0 mm, was used for preliminary experiments. A medium fraction, 0.5 to 1.0 mm, was used for the majority of the experiments. The sand was poured into glass chromatography columns with a length of about 500 mm and an internal diameter of 25 mm. The sand was supported by a fritted glass disk. Each column had a 24 × 40 female ground glass joint at its top and a stopcock at its bottom.

A column was packed by pouring dry sand into the column. A 55 mm headspace was left in the column. To prepare experiments with water-wetted sand, water was slowly introduced into the bottom of the column using a buret connected to the column. Then the column was drained for about 3 hours to bring the column into near field capacity conditions. A glass reducing adapter with a male 24 × 40 and a female 14 × 35 ground glass joint was modified to serve as the air inlet and outlet at the top of the column as shown in Figure 2. A small glass tube with a 4 mm ID was sealed into the side of the adapter. This tube was bent and extended about 5 mm beyond the end of the male joint. In experiments with water-wetted sand, a glass drying tube filled with indicating silica gel desiccant was inserted into the outlet of the modified reducing adapter. Silica gel has a low affinity for hexane vapors. A 10 mm ID glass tube with 14 × 35 male and female glass joints and an overall length

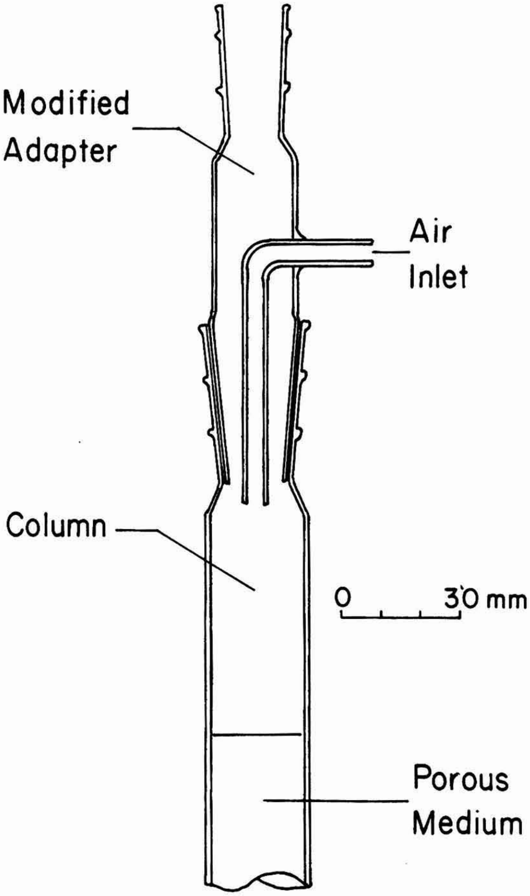

FIGURE 2 Schematic of the experimental apparatus showing a portion of the column and the modified reducing adapter.

of 275 mm was inserted into either the modified adapter or the drying tube. Finally a 10 mm ID glass tube with one 14 × 35 male glass joint and an overall length of 160 mm was inserted into the longer tube. These tubes were packed with activated carbon, held in place with glass wool plugs. The tubes served as carbon traps to adsorb hexane leaving the column. All ground glass joints were coated with high vacuum silicon grease to minimize losses of vapors.

Hexane, consisting of 85.6% *n*-hexane and 14.4% other hexane isomers, was chosen for the experiments due to its high equilibrium vapor pressure, 16.0 kPa at 20°C, and its low aqueous solubility, 9.5 mg L^{-1} at 20°C [*9*]. In experiments with water-wetted sand, the hexane was dyed with Morton Thiokol Automate Blue 8, #7121, a xylene-based dye that is insoluble in water.

Air was first pulled through a preliminary activated carbon filter to remove organic compounds present in the ambient air. In experiments with dry sand, the air also passed through a desiccant to remove water vapor. In experiments with water-wetted sand, the air passed through a water-filled midget impinger to humidify the air stream. Then the air flowed through the small inlet tube in the modified reducer at the top of the column. The air with hexane and any water vapor that diffused from the column flowed through the drying tube, if present, and the two activated carbon traps. The experiments were conducted in a constant temperature chamber at 25°C.

At the end of each test, the activated carbon was poured into a glass vial containing carbon disulfide The vial was sealed with a Teflon-lined plastic cap. The concentration of *n*-hexane in the solution was determined using a gas chromatograph with flame ionization detector [*10*].

A series of preliminary experiments was conducted to determine the effect of the air flow rate on the diffusion of hexane from the column. These tests used a dry sand, 1.0 to 2.0 mm, which was coarser than the sand used in the remaining experiments. Two mL of hexane, corresponding to a spill depth of approximately 4 mm, was spilled on the sand. The column was sealed with the adapter and carbon traps. A constant flow of air was pulled through the system at flow rates ranging from 0.05 to 0.7 L $\min^{-1}$ in individual experiments. After 35 minutes, the carbon traps were removed and the mass of hexane trapped was determined. Several additional experiments were conducted with hexane and no sand. In subsequent tests, the air flow was regulated to 0.55 L $\min^{-1}$ with a 24 gage hypodermic needle serving as a critical flow element [*11*].

To determine the tortuosity of dry sand, hexane vaporization experiments were conducted. A buret filled with hexane was connected to the bottom of the column. Hexane was introduced into the column until 2.2 mL had flowed above the frit. The air flow was started. The distance from the top of the capillary fringe to the top of the sand was measured periodically. The carbon traps were also changed periodically. The hexane captured was quantified. The experiments were conducted until a steady-state flux was observed.

Similar tests were conducted with sand at near field capacity with water. Since water filled the entire pore space in the capillary fringe, a vacuum was momentarily applied to the bottom of the column to suck out much of this capillary water. Then hexane was introduced into the bottom of the column as in the tests with dry sand.

Spill experiments were conducted by sprinkling a known volume of hexane uniformly onto the top of the sand. Spill volumes were 4.9 mL for dry sand and 3.5 mL for water-wetted sand, corresponding to approximately 10 mm and 7 mm layers in an empty column. Observations of the penetration depth of the hexane and the depth of the evaporating front of hexane were made over time. In water-wetted sand, the location of this front was determined by a change in the appearance of the dye in the column. The carbon traps were changed at intervals that varied as a function of the expected hexane evaporated.

The air-filled porosity of dry sand was determined by measuring the volume of water required to saturate a given volume of sand. This air-filled porosity for experiments conducted in dry sand was determined for individual columns at the end of the experiment when all hexane had evaporated.

The air-filled porosity of water-wetted sand was determined by taking samples of the moist sand with a thin-walled steel tube. The water content of these samples was determined gravimetrically by determining the difference in mass before and after drying the sand at 100°C. Since these measurements were conducted after the flux measurements, their accuracy is based on the assumption that there was little change in the water content after the initial displacement due to the hexane spill.

RESULTS AND DISCUSSION

The average value for the diffusion coefficient of hexane in air at 25°C determined in the Stefan tube experiments was 0.082 cm^2/s. This is slightly higher than the 0.076 cm^2/s value computed using the theoretical equation using the Lennard-Jones potential [*8*].

To determine the effect of air flow rate on the rate of diffusion of the hexane vapors, 2 mL of hexane was spilled on dry, coarse sand. In addition, several tests were conducted with hexane and no sand. The mass of hexane trapped in the first 35 minutes was determined. The amount of *n*-hexane trapped for the tests without sand increased linearly over a flow range of 0.05 to 0.2 L $\min^{-1}$. For the tests with sand, the mass of hexane trapped initially increased with flow rate but leveled off at an air flow rate of about 0.35 L $\min^{-1}$. This corresponds to about 13 headspace changes per minute. Since there was essentially no change in hexane trapped at higher flow rates, it was assumed that this flow was sufficient to minimize air-phase resistance in these tests. An air flow rate of 0.55 L $\min^{-1}$ was used in subsequent experiments.

The tortuosity for dry sand was determined by measuring the steady-state flux of *n*-hexane diffusing through a known path length of dry sand in the column. The average value of tortuosity was 1.73 at an air-filled porosity of 0.40. This is higher than the value of 1.37 predicted using Equation 3. Similar experiments were conducted for sand at near field capacity for water. In these tests, the capillary fringe of water was quickly sucked out of the bottom of the column to give an air-filled diffusion path through the entire column. Then hexane was introduced into the bottom of the column. The steady-state flux of *n*-hexane was measured. After all hexane had evaporated, samples of the sand were taken to determine the air-filled porosity as a function of depth. To compare the measured flux with theoretical, steady-state predictions, the column was assumed to be

8 discrete segments of uniform length. The experimental air-filled porosity and dry sand tortuosity were used with Equation 4 to estimate the tortuosity of each segment. The steady-state flux predicted for diffusion across the 8 segments in series was within 5% of the experimental flux. This agreement supports both the use of Equation 4 to correct the tortuosity and the measurements of air-filled porosity made after the experiment.

In the spill experiments, 4.9 mL and 3.5 mL of hexane were spilled onto dry and water-wetted sand, respectively. The infiltration of hexane was measured as a function of time. The infiltration front achieved about 80% of its final value in two to three hours. In addition, the hexane concentrations appeared to be higher at the top of the column than at the bottom. Therefore, the assumptions in Thibodeaux's model that the infiltration occurred instantaneously and that hexane distribution was uniform were not strictly satisfied.

Figure 3a shows the ratio of the experimental value to theoretical predictions of the diffusion path length, $(h - y)$, for the experiment with initially dry sand. Since the hexane did not reach the bottom of the column instantaneously, this ratio is given for both fixed values of h equal to 450 mm and the observed values of h. The theoretical path length, $(h - y)$, using either method of specifying h is greater than observed values at the beginning of the experiment and is less than observed path length at the end. This is consistent with the observations that the concentration of hexane was higher at the top of the column than at the bottom. Figure 3b shows the ratio of experimental flux, J_{exp}, to the theoretical flux, J_{th}, versus time based on the empirical value of $(h - y)$. Except the first few hours, the ratio was close to unity for the first 6 days of the experiment. At this time, liquid hexane could no longer be observed in the column and essentially all the hexane introduced had been captured. Replicate tests were conducted with water-wetted sand. Figure 4a shows the ratio of the experimental value to theoretical predictions of the diffusion path length, $(h - y)$, for the experiment with initially water-wetted sand. This ratio is shown for both fixed values of h equal to 450 mm and the observed values of h. In these experiments, the ratio varied from about 0.8 to 0.9 except during the first few hours of the experiment. Figure 4b shows the ratio of experimental flux, J_{exp}, to the theoretical flux, J_{th}, versus time. Except during the first few hours, the ratio was close to unity for the first 4 to 5 days. Results from a replicate experiment were very similar to those shown in Figure 4.

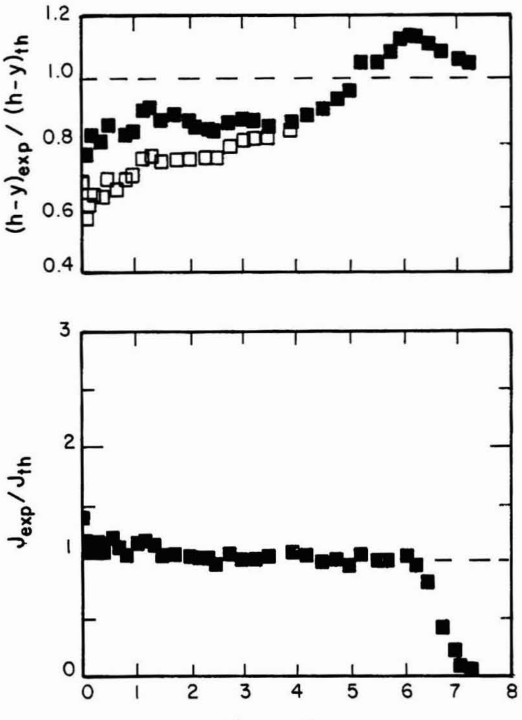

FIGURE 3 Data from a spill on initially dry sand: (a) the ratio of experimental to theoretical values of path length, $(h - y)$. Theoretical values of $(h - y)$ based on a constant value of *h*—— □ and on empirical values of *h*—— ■; (b) the ratio of experimental flux to theoretical flux.

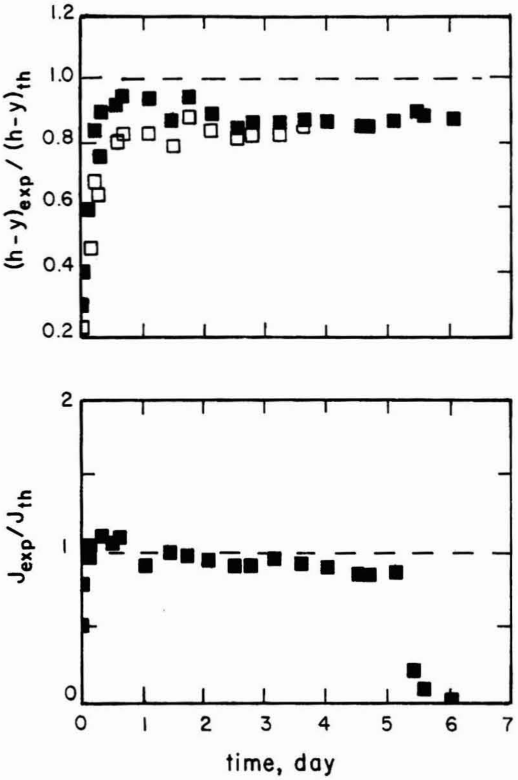

FIGURE 4 Data from a spill on water-wetted sand from two experiments: (a) the ratio of experimental to theoretical values of path length, $(h - y)$. Theoretical values of $(h - y)$ based on a constant value of *h*—— □, and on empirical values of *h*—— ■; (b) the ratio of experimental flux to theoretical flux.

CONCLUSIONS

Simple laboratory experiments to simulate a spill of a volatile liquid on a sandy soil were conducted. In these experiments, hexane was spilled onto both initially dry sand and water-wetted sand at near field capacity. The hexane emitted from the sand was trapped onto activated carbon, and its mass was determined by gas chromatography.

The experimental conditions approximated the assumptions of a theory developed by Thibodeaux [*3*]. Predictions of a modification of this model were generally in good agreement with the volatilization data supporting the use of this model to predict the air emissions due to a spill of a liquid onto sandy soils. Since the model ignores competing mechanisms such as sorption of the liquid or its vapors, chemical and biochemical reactions, and solubilization, its use should be restricted to the early portions of such a spill and should not be used when the other processes are of similar importance.

ACKNOWLEDGEMENT

This research was conducted by Mukul Sharma and Thomas J. Overcamp at Clemson University. It was supported in part by the U.S. Department of the Interior, Geological Survey, through the South Carolina Water Research Institute.

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Biological Conversion of Hydrogen Sulfide into Elemental Sulfur

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Currently, hydrogen sulfide is removed from process gas streams by a series of reactions at high temperature to produce elemental sulfur in Claus, Stretford or other processes. These physicochemical processes have high intrinsic capital and operating costs, often are restricted by contaminants, and do not effectively remove all the H_2S. As an alternative, the anaerobic, photosynthetic bacterium, Chlorobium thiosulfatophilum, has been demonstrated to convert hydrogen sulfide to elemental sulfur in a single step at atmospheric conditions. The autotrophic bacterium uses CO_2 as the carbon source. Energy for cell metabolism is provided by incandescent light and the oxidation of H_2S. A bench scale study has been performed in a CSTR equipped with a sulfur separator. Optimum process conditions have been achieved to maximize cell growth and elemental sulfur production. Near total conversion of H_2S is achieved in a retention time of a few minutes. High concentrations of H_2S or organics do not affect the culture. Sulfur recovery by settling is very efficient and near theoretical yields of sulfur are achieved. Economic projections indicate that sour gas can be desulfurized for \$ 0.08-0.12/MSCF.

INTRODUCTION

Natural gas pipelines traverse most of the United States and provide one-fifth, or about 18 quads, of our total energy needs today. The gas delivered to homes must have a high heating value and must be free of toxic gases, such as H_2S. Much of our known gas reserves contain significant quantities of inert gases (CO_2 and N_2) or H_2S, and are considered low-quality natural gas (LQNG). Furthermore, 37 percent of future discoveries are expected to be LQNG, with almost 80 TCF contaminated with H_2S [*1*].

Removal of these contaminants from natural gas is expensive, especially when large amounts of N_2 are present [*2, 3*]. Treatment involves absorption of the acid gases (CO_2 and H_2S), usually in amine scrubbers, followed by stripping to regenerate the solvent. The concentrated stream of H_2S and CO_2 is then introduced into a Claus unit where H_2S is burned to SO_2, which is then reacted catalytically with additional H_2S to produce elemental sulfur.

This process produces a valuable by-product, sulfur, and treatment can be justified for large reserves. However, conversion of more than 95 percent of the H_2S to sulfur is quite expensive and large quantities of SO_2 and H_2S remain as pollutants. Furthermore, the process is energy and capital intensive [*4*], and is not appropriate for small-scale LQNG reserves, where most of the future discoveries are expected.

Clearly, the nation needs a simple technology that can be economically applied to LQNG in small quantities. Such a process will reduce future energy costs and move the nation closer to energy self-sufficiency.

BIOLOGICAL REMOVAL OF H_2S

Bacteria may be used to convert H_2S in LQNG to either elemental sulfur or sulfate as the final product. Biological conversion can be quite efficient and, as will be shown later, is much less capital intensive than traditional technology. Bacteria capable of metabolizing H_2S may be classified into three major groups:

- aerobic sulfate producers
- anaerobic sulfate producers
- anaerobic elemental sulfur producers

Aerobic bacteria require oxygen for growth which could result in flammable concentrations when mixed with natural gas [*5*]. Anaerobic sulfate production is quite slow and requires large amounts of nitrate for H_2S removal [*6*]. Also, sulfate is difficult to separate and has a low value. Consequently, this project has concentrated on the anaerobic production of elemental sulfur, which is easily recovered from the bioreactor by gravity settling.

Hydrogen sulfide can be converted to sulfur by photosynthetic sulfur bacteria according to the equation:

$$2H_2S + CO_2 \xrightarrow[\text{light}]{} 2S + \underset{\text{biomass}}{(CH_2O)} + H_2O \qquad (1)$$

In using the bacterium *Chlorobium thiosulfatophilum*, sulfur is deposited outside the cell membrane where it is collected as a finely divided powder [*7*]. In addition, biomass or single cell protein (SCP) is produced as a valuable by-product for use as an animal feed. High concentrations of H_2S (> 15 percent) enhance the reaction rate, so that the technology applies to a broad range of H_2S concentrations in LQNG [*8*]. The reaction is irreversible (extracellular sulfur is not utilized) and there are no equilibrium constraints; therefore, high conversions can be achieved. Others have found that these bacteria utilize intracellular sulfur to produce sulfate when H_2S is deficient [*8*]. Bioengineering Resources (BRI) has developed technology to avoid such secondary metabolism by insuring adequate mass transfer of gaseous substrates. The presence of other gases, such as N_2 or CH_4, have no adverse effects upon the reaction. This process also converts some of the CO_2 present into animal feed and will therefore reduce emissions of greenhouse gases.

The biological process for H_2S removal from LQNG using *C. thiosulfatophilum* and the production of sulfur is quite simple. The gas is bubbled through a bioreactor containing a culture of bacteria that carry out the reaction of Equation (1). H_2S is dissolved in the aqueous medium in the reactor and then is metabolized by the photosynthetic bacteria to produce sulfur. The methane and other gases leave the bioreactor and can be introduced into the pipeline. Sulfur would be separated by gravity from the reactor effluent and marketed. There are no other chemical by-products from the reaction that must be separated or recovered. The excess biomass can be harvested and marketed as single-cell protein, which has a value of about $220 per ton (the current soy bean price) as an animal feed ingredient.

The reaction takes place at ambient temperature with high energy efficiency. Biocatalysts are tolerant of many toxic substances and species of *Chlorobium* have been used in our laboratory with synthesis gas, which is much more toxic than natural gas. Furthermore, the biocatalyst is continuously and automatically regenerated by cell growth in the reactor. Stoichiometric amounts of elemental sulfur are produced and the sulfur is readily recovered by settling.

PURPOSE

The purpose of this paper is to present steady state results from stirred tank reactor studies using *C. thiosulfatophilum*, with and without sulfur recovery. The objective of these studies was to define the required gas retention time (defined as the ratio of the culture volume to gas flow rate) for complete sulfur removal from LQNG. In addition, process economics are projected for removing H_2S and recovering elemental sulfur from gas streams containing 2.5 and 1.0 percent H_2S.

MATERIALS AND METHODS

Chlorobium thiosulfatophilum (ATCC 17092) was obtained from the American Type Culture Collection (Rockville, MD). It was grown on a basal medium containing (per 1l): yeast extract (Difco), 5.0 g; Pfennig's minerals solution [9], 50 ml; Pfennig's trace metals solution [10], 1 ml; B-vitamin solution, 5 ml; and sodium bicarbonate, 4.0 g.

The continuous stirred-tank reactor used was a New Brunswick Scientific (Edison, NJ) BioFlo C30 fermenter. The fermenter was modified to operate under strict anaerobic conditions with both continuous gas and liquid flow. The liquid working volume was 1250 ml and the overhead gas volume was 750 ml. Illumination necessary for growth was supplied by two 200 W tungsten lights (120° apart) directed toward the glass fermentation vessel from a distance of approximately 15 cm. Experiments were carried out at 30°C and pH 7.5. The feed gas used was a mixture of H_2S, CO_2, CH_4 and He (2.5/10.0/15.0/72.5%v/v) and was continuously fed to the reactor at atmospheric pressure. A schematic of the equipment is shown in Figure 1. A 475 ml separatory flask with a side arm was used for the rapid separation of solid sulfur from the recycle liquid stream. The separator recycle loop was removed for those experiments performed without sulfur recovery.

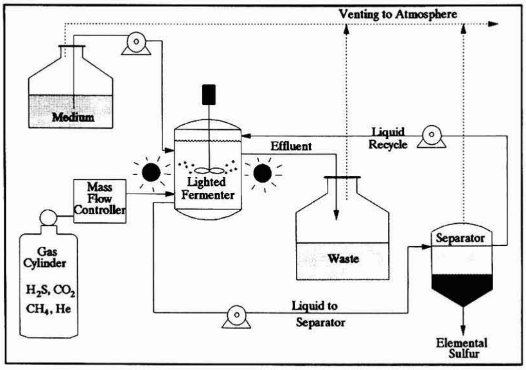


FIGURE 1 Schematic of hydrogen sulfide CSTR system.

Liquid and gas samples were withdrawn anaerobically from the reactors during cultivation and analyzed for liquid and gas phase concentrations. The dry cell weight concentration was obtained by centrifuging 1 ml of liquid sample for 2 min at 7000 rpm, discarding the top phase and resuspending the cells in 1 ml of methanol to extract chlorophyl. After an additional centrifugation cycle, the green colored methanol extract was combined with 1.5 ml of fresh methanol. The absorbance was measured at 670 nm on a Shimadzu UV-1201 spectrophotometer (Shimadzu Corp., Kyoto, Japan) and converted to dry weight cell concentration using a calibration curve.

Sulfide in the liquid phase was measured in sulfide antioxidant buffer (SAOB) using an Orion silver/sulfide electrode (Orion Res. Inc., Boston, MA) and an Orion double junction reference electrode in conjunction with an Orion Benchtop pH/ISE meter, model 710A (Orion Res. Inc., Boston, MA). The samples in the SAOB buffer were frozen to stop microbial activity until sulfide analyses were performed. Sulfur in the liquid sample was settled by centrifugation, and then mixed with acetone. The acetone was then evaporated and the dried sulfur was dissolved in chloroform. The concentration of elemental sulfur was determined spectrophotometrically at 290 nm in combination with a standard curve [11]. Sulfate in the liquid sample was measured turbidimetrically at 420 nm using a standard curve prepared with sodium sulfate solution [12]. Conditioning reagent (0.25 ml) was first added to a 5.0 ml aliquot of the centrifuged sample. After stirring the solution, 1.0 ml of 0.24 g ml^{-1} $BaCl_2$ solution was added to initiate the reaction to $BaSO_4$.

Gas analyses were performed on a gas chromatograph (Perkin Elmer 8500 gas chromatograph, Norwalk, CT) using a 3 mm × 1.8 m PTFE column packed with Chromosorb 107, 80/100 mesh (Alltech, Deerfield, IL). The oven temperature was maintained at 80°C, while the injector and thermal conductivity detector temperatures were 130°C and 200°C, respectively. Helium at 28 ml min^{-1} was used as the carrier gas. Light intensities were measured with a LX-101 digital lux meter (Cole-Parmer, Chicago, IL).

TABLE 1. Steady State Data for the Conversion of H_2S to Elemental Sulfur by *Chlorobium thiosulfatophilum*. No Sulfur Recovery

Gas RT (min)	OD670	% H_2S Conversion	SO_4^{2-} mg l^{-1}	S^0 mg l^{-1}	S^{2-} mg l^{-1}
13.7	1.186	58.39	62	765	55
15.3	1.180	64.55	55	688	43
16.4	1.406	70.63	54	456	31
25.8	1.155	98.89	31	436	1
30.8	0.564	100.00	58	86	2
39.8	0.410	100.00	143	28	0

Reaction Conditions:
Temperature: 30°C
pH: 7.5
Light: Two 200 W Lamps
Liquid Dilution Rate: 0.047 hr^{-1}

TABLE 2. Steady State Data for the Conversion of H_2S to Elemental Sulfur in a CSTR with Sulfur Recovery Using *Chlorobium thiosulfatophilum*

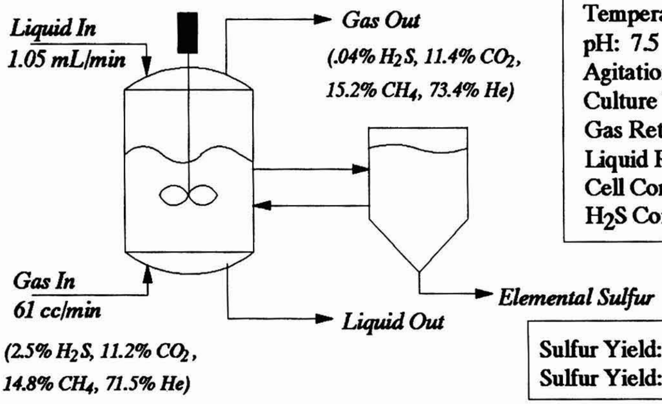
Gas RT (min)	OD670	% H_2S Conversion	SO_4^{2-} mg l^{-1}	S^0 mg l^{-1}	S^{2-} mg l^{-1}
12.2	2.427	53.42	89	11	119
14.0	2.743	76.99	60	49	57
15.2	2.649	81.70	46	54	38
15.5	2.641	88.30	36	86	24
16.6	2.661	89.75	53	76	30
18.7	2.028	90.11	44	63	25
20.6	1.403	98.50	47	116	0
22.1	1.105	96.6	42	74	2
23.9	0.986	100	35	63	1
28.3	1.147	100	92	119	0
31.4	2.054	100	414	90	0
40.7	1.791	100	310	80	0

Reaction Conditions:
Temperature: 30°C
pH: 7.5
Light: Two 200 W Lamps
Liquid Dilution Rate: 0.047 hr^{-1}

RESULTS AND DISCUSSION

Continuous Reactor Studies

Continuous stirred tank reactor studies were performed with *C. thiosulfatophilum* to obtain steady state operating data for the production of elemental sulfur from H_2S. Table 1 shows steady state data for the system without sulfur recovery as a function of gas retention time. The liquid retention time in these studies was 0.047 hr^{-1}. As is noted in the table, the H_2S conversion ranged from 58 percent at a gas retention time of 13.7 min to 100 percent at a gas retention time of 30 min. Essentially no sulfide was observed



Culture: *Chlorobium thiosulfatophilum*
Temperature: 30°C
pH: 7.5
Agitation rate: 500 rpm
Culture Volume: 1250 mL
Gas Retention Time: 20.6 min
Liquid Retention Time: 19.8 hr
Cell Concentration (as OD): 1.4
H_2S Conversion: 98.5%

Sulfur Yield: 1 mole S^o/mole H_2S consumed
Sulfur Yield: 99.2% of theoretical

Material Balance, mmol/hr

	Gas In	Liquid In	Gas Out	Solid Out	Liquid Out
H_2S	4.06	0.0	0.06	0.0	0.0
CO_2	18.48	3.00	18.23	0.0	1.25
CH_4	24.35	0.0	24.35	0.0	0.0
He	117.70	0.0	117.70	0.0	0.0
S^{2-}	0.0	0.0	0.0	0.0	0.0004
SO_4^{2-}	0.0	0.0	0.0	0.0	0.03
S^0	0.0	0.0	0.0	3.74	0.23

FIGURE 2 Material balance and operating conditions for the conversion of hydrogen sulfide to elemental sulfur by *C. thiosulfatophilum*.

in the liquid phase at gas retention times greater than 25 min, indicating complete H_2S removal. Elemental sulfur was the predominant product (93–95 percent of the product), except when the H_2S concentration fell to zero and the culture had to utilize sulfur in place of sulfide as a source of electrons.

Table 2 shows steady state data for the CSTR system with sulfur recovery as a function of gas retention time. The liquid retention time in these initial studies was also 0.047 hr^{-1}. As is noted in Table 2, the H_2S conversion ranged from 53 percent at a gas retention time of 12.2 min to 100 percent at a gas retention time of 23.7 min. Essentially no sulfide was observed in the liquid phase at gas retention times greater than 20 min. Elemental sulfur was again the predominant product, except when the H_2S concentration fell to zero and the culture had to utilize sulfur in place of sulfide as a source of electrons. These data show a definite improvement over the data without sulfur recovery. By contrast, a 30 min gas retention time was required for 100 percent sulfur removal without sulfur recovery.

Figure 2 shows a material balance and operating conditions for the conversion of 2.5 percent H_2S in a gas stream to elemental sulfur by *C. thiosulfatophilum.* As was noted earlier, a 20 mn gas retention time is required to attain a 98.5 percent H_2S removal. The sulfur recovered from the process is 99.2 percent of the theoretical yield of 1 mole sulfur per mole of H_2S consumed.

ECONOMIC PROJECTIONS

Based upon the results of the continuous reactor studies, economic projections were prepared for converting 50 million SCFD of natural gas containing H_2S to elemental sulfur and SCP. The process is essentially identical to the process described previously in Figure 1. Two gas stream H_2S concentrations were considered:

- 2.5 percent H_2S in natural gas
- 1.0 percent H_2S in natural gas

The capital costs for treating 2.5 percent H_2S in natural gas are summarized in Table 3. The fixed capital investment including the reactor system, sulfur recovery, cell recovery and offsites total $18.13 million. The economic analysis for this case, shown in Table 4, shows that 20,000 tons of sulfur and 9,400 tons of SCP are generated per year for a credit of $3.1 million/yr. The operating costs including raw materials, utilities, labor, maintenance, depreciation and taxes and insurance total $4.6 million/yr. The net cost of treating the gas is $0.12 per thousand cu. ft. If 1 percent H_2S in natural gas is treated, the fixed capital investment decreases to $8.6 million as is shown in Table 5, and the net cost of gas treating decreases to $0.08 per thousand cu. ft, as is shown in Table 6. By contrast, a Claus recovery process including scrubbing and adsorption for treating 50 million SCFD of natural gas containing 2.5 percent H_2S would require a capital investment of $70 million. The manufacturing cost would be $439 per ton of sulfur [*13*].

TABLE 3. Fixed Capital Investment

BIOLOGICAL H_2S REMOVAL
50 million CFD - 2.5 percent H_2S

Equipment Item	Capital Cost M$
Reactor System	10,050
Sulfur Recovery	480
Cell Recovery	1,300
Off-site Facilities	6,300
Total	18,130

TABLE 4. Economic Analysis

BIOLOGICAL H_2S REMOVAL
50 million CFD - 2.5 percent H_2S

Cost Item	Cost, M$/yr
Raw Materials	890
Utilities	150
Labor/Supervision/Fringe	550
Maintenance, 5% FCI	910
Depreciation, 10% FCI	1,810
Taxes, Insurance, 2% FCI	360
Total	4,670
Credits: Sulfur - 20,000 TPY @ $50 per ton	1,000
SCP - 9,400 TPY @ $220 per ton	2,070
Net Manufacturing Cost	1,600
Net Cost of Gas Treating	$0.12/MSCF

TABLE 5. Fixed Capital Investment

BIOLOGICAL H_2S REMOVAL
50 million CFD - 1.0 percent H_2S

Equipment Item	Capital Cost M$
Reactor System	4,200
Sulfur Recovery	340
Cell Recovery	720
Off-site Facilities	3,380
Total	8,640

TABLE 6. Economic Analysis

BIOLOGICAL H_2S REMOVAL
50 million CFD - 1.0 percent H_2S

Cost Item	Cost, M$/yr
Raw Materials	360
Utilities	60
Labor/Supervision/Fringe	550
Maintenance, 5% FCI	430
Depreciation, 10% FCI	870
Taxes, Insurance, 2% FCI	170
Total	2,440
Credits: Sulfur - 7,800 TPY @ $50 per ton	390
SCP - 3,660 TPY @ $220 per ton	810
Net Manufacturing Cost	1,240
Net Cost of Gas Treating	$0.08/MSCF

CONCLUSIONS

The anaerobic bacterium *C. thiosulfatophilum* has been shown to be very effective in removing H_2S from gas streams and converting it to elemental sulfur. A 20 min gas retention time is required to completely remove the H_2S from a gas stream containing 2.5 percent H_2S at 1 atm. The sulfur recovered from the process by gravity separation was 99.2 percent of the theoretical yield of 1 mole sulfur per mole of H_2S consumed.

The economics of biologically converting H_2S in natural gas to elemental sulfur and SCP are potentially quite attractive. Economic projections show that the H_2S can be removed from sour gas for as little as $0.08 per thousand cu. ft. of gas.

ACKNOWLEDGMENT

The work presented in this paper was made possible through the financial support of the U.S. Department of Energy, Morgantown Energy Technology Center, under grant number DE-FG05-93ER81484.

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SO_2 Oxidation in a Periodically Operated Trickle Bed: Comparison of Activated Carbon Catalysts

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Catalytic activities of two different activated carbons, BPL™ and Centaur™ catalysts (Calgon Carbon Corp.), were compared in a periodically operated trickle-bed reactor for SO_2 oxidation by varying the cycle period and split. In an effort to characterize the carbon surface, differential thermogravimetric analysis and TPD were used to observe oxygen functional groups. The Centaur catalyst, which appears to have a more suitable density of oxygen functional groups, has the higher catalytic activity for SO_2 oxidation.

INTRODUCTION

The use of activated carbon in a trickle bed reactor for SO_2 cleanup of stack gases offers a low-temperature operation and low cost as well as the environmental advantage of producing no solid wastes or liquid while removing better than 95% of the gaseous SO_2 from the stack gases. SO_2 oxidation over activated carbon involves the reaction between SO_2 chemisorbed on active centers with chemisorbed molecular oxygen to form SO_3 that remains adsorbed on the catalyst surface at low temperatures. The active sites may be regenerated in two ways in order to remove the SO_3 from the carbon. One of these uses a two-phase moving bed reactor. An example is the B-F process [*1*]. The activated carbon is regenerated by thermal desorption at 400°C, producing concentrated SO_2 or SO_3. Carbon loss through attrition in the moving bed and CO_2 formation in regeneration are significant costs for the process.

The second method, which uses a trickle bed for SO_2 adsorption and oxidation, regenerates the carbon by washing with water (or dilute H_2SO_4). Sulfuric acid is the only product in this method. Attrition loss is eliminated and there appears to be negligible carbon consumption [*2*]. If periodic liquid flow flushing in place of continuous water flow is used, a large increase in the oxidation rate and a sharp decrease in the pressure drop are observed [*3, 4*].

The performance of a trickle-bed reactor can be influenced by several factors. Of prime importance are gas-liquid-particle mass transfer and the fraction of the outer surface of the catalyst particles covered by flowing liquid. Nevertheless, previous studies [*3, 5*] indicate that the activity of the carbon in the trickle bed depends on the variety of the carbon. In the present study, we consider the question of carbon choice. A carbon widely used in the past is compared with a newly developed material that is reputed to be unusually active for SO_2 oxidation. Performances of these carbons in a periodically operated trickle bed are compared and TPD-DTA measurements are used to explain the results obtained.

It is our hypothesis that performance differences are caused by the surface properties of the two carbons, since surface areas and void volumes are similar for both materials. Oxygen functional groups are thought to adsorb SO_2 as the first step in oxidation [*6*].

In general, surface oxygen structures are stable at temperatures below 200°C, but when heated at higher temperatures in an inert atmosphere, decompose to produce CO_2 and CO. Thus, the quantity of surface oxygen functional groups on activated carbons can be evaluated by temperature programmed desorption (TPD). Also, the numbers of such groups can be monitored indirectly by means of differential thermogravimetric analysis (DTA).

EXPERIMENTAL

SO_2 Scrubbing System

In a trickle bed scrubber, a carbon is used to adsorb SO_2 and oxidize it to SO_3. The SO_3 is strongly adsorbed on active sites on the catalyst, inhibiting them from participating in oxidation catalysis until the SO_3 can be removed, by flushing the carbon with water to produce H_2SO_4.

As can be seen from Figure 1, the experimental scrubber incorporates a reactor system, a gas supply system, a water

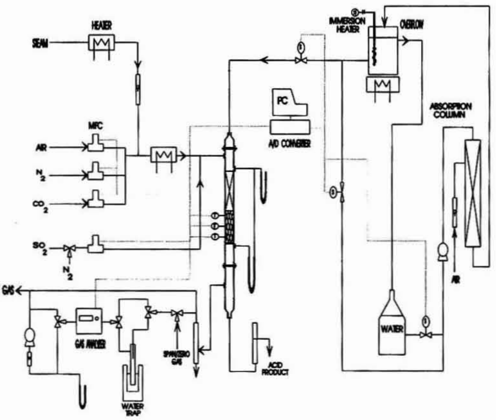

FIGURE 1 Schematic diagram of a periodically operated trickle-bed SO_2 oxidation reactor.

supply and recirculation system, and an analysis and control system. The reactor consists of a thick glass tube, 60 cm in height and 5 cm in diameter. At the top is a Teflon™, acid-resistant distributor. To mix the gas and liquid phases well, the top part of the reactor is filled with tiny, 1.6-mm glass beads, below which lie packed carbon particles supported on a Teflon™ screen. Within the catalyst bed, 0.2-mm type-K thermocouples are located at its top, middle, and bottom. Three thermocouples are evenly spaced and connected to a computer through an interface to record the temperature. Above and below the catalyst bed are manometer ports for measuring pressure drop. The reactor is wrapped with insulation and heating tape to keep it at 80°C. Gas and liquid enter through the top of the reactor, flow downward, and are separated at the bottom. The gas leaves through a side port while the liquid passes out a drain at the bottom, above which liquid is maintained to serve as a gas seal.

The simulated stack gas was used for the experiments, prepared as shown in Figure 1. The mixture of air, N_2, and CO_2 was heated to about 120°C, injected with steam, and then combined with SO_2.

The water circulation system consisted of a 50-L borosilicate glass head tank used to feed the trickle bed. The tank was maintained at 80°C by a stirrer-hot plate. The water feed to the head tank was saturated with air in a co-current down-flow trickle bed. Computer-controlled solenoid valves initiated the periodic water feed to the main activated carbon-filled bed. A peristaltic pump circulated water from the bottom of the holding tank (Figure 1), through the saturator and into the overhead tank. Overflow from the head tank was returned to the holding tank.

Analyses were performed using a SO_2 gas analyzer, and an auto-titrator for the liquid samples collected from the bottom of the trickle bed. The gas analyzer was a UV spectrometer (Western Research, Calgary, Alberta), so that SO_2 concentrations leaving the trickle bed in the gas phase were measured continuously. Sulfuric acid concentrations in the liquid samples were determined using an auto-titrator. A computer monitored temperatures, mass flows and SO_2 concentrations. It also set the mass flow controller and initiated solenoid valve actions.

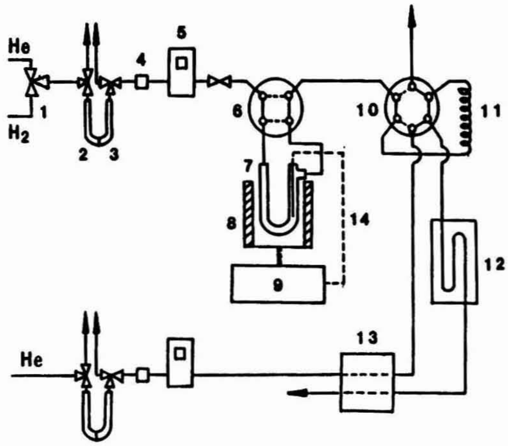

FIGURE 2 Schematic flow diagram of TPD apparatus. 1, 3-way valve; 2, oxygen trap; 3, moisture trap; 4, gas filter; 5, mass flow controller; 6, 4-port valve; 7, reactor; 8, furnace; 9, thermocouple programmer; 10, 6-port valve; 11, sampling loop; 12, column; 13, TCD; 14, thermocouple.

Characterization of Carbons

The surface areas of the carbons were obtained by nitrogen adsorption at 77 K using the BET equation. Adsorption was carried out in an Autosorb-1. An equilibrium time of 2 min was allowed for each adsorption point. Before adsorption measurement, each carbon sample was outgassed at 200°C and 3 torr for 18 h.

Decomposition of the surface oxygen functional groups of the activated carbons was carried out by temperature programmed desorption (TPD), the apparatus for which is shown schematically in Figure 2. TPD plots were obtained by flowing 10 mL (STP)/min of helium over the 0.1 g carbon sample as the temperature was raised at a rate of 10°C/min. A temperature controller was used to raise the temperature linearly at 10°C/min between 100 and 1000°C. The reactor was made up of a quartz tube 5 mm inside diameter and 50 cm long, with a long, tortuous preheating zone.

Identification of the carbon oxides evolved on thermal decomposition was undertaken by gas chromatography with a Porapak™ Q column at 40°C. The oxygen functional groups were indirectly evaluated by DTA.

Experimental Design

The two catalysts under study were BPL™ and Centaur™ carbon catalysts from Calgon Carbon Corp. The same mass of catalyst (178 g) was used in all experiments even though Centaur catalyst is more compact than the BPL catalyst. Details of the properties of the carbon catalysts are summarized in Table 1.

The simulated flue gas had a volumetric composition 10% CO_2, 10% H_2O, 5% O_2 and 2500 ppm SO_2, the remainder being N_2. A 1000 h^{-1} space velocity was used.

The performance of trickle-bed for SO_2 scrubbing was determined for each carbon over a range of periods and splits. Period is defined as the time that elapses between repetitions of the same input condition. Split is the fraction

TABLE 1. Properties of Activated Carbon Catalysts

Catalyst	BPL	Centaur
Activation method	high-temperature steam	exposure to a nitrogen-containing compound during high temperature activation [8]
Particle size range	4/10 US mesh	4/8 US mesh
Ash (wt. %)	6	4
Apparent density (g/mL)	0.48	0.58
BET surface area m^2/g)	699	665

of the cycle period during which water flushes the bed. Period was varied from 15 to 60 min and split from 0.0083 to 0.2. All other variables such as superficial liquid velocity, gas space velocity, feed gas compositions and temperatures were held constant.

RESULTS AND DISCUSSION

Variation of SO_2 Concentration and Temperature within a Cycle

Figure 3 compares SO_2 removal for the Centaur and the BPL catalysts for a cycle time of 30 min and flush time of 1.5 min. Superficial liquid velocity was ca. 0.2 cm/s; liquid and gas temperatures, 80°C; carbon mass in the trickle bed was 178 g; and space velocity was 1000 h^{-1}. As can be seen, there are two parts to the cycle: the brief part represents flushing the bed with water, while during the longer part of the cycle, only gas flows over the initially wetted carbon. The SO_2 profiles of the two carbons appear quite different: the SO_2 concentration profile for Centaur carbon (Figure 3a) shows a rounded shoulder near the mid-point of each cycle in the SO_2 emerging from the bottom of the trickle bed, whereas for the BPL carbon (Figure 3b) there is a sharp rise and fall that begins when water is introduced but peaks after the water flow has been interrupted.

There is also an important difference in scrubber performance with the two carbons. The mean outlet SO_2 is between 40 and 50 ppmv for the Centaur carbon. This corresponds to better than 98% SO_2 removal. On the other hand, the mean outlet SO_2 lies between 250 and 350 ppmv for the BPL carbon which represents 85 to 90% SO_2 removal.

The transit lag from the bottom of the trickle bed to the SO_2 detector is estimated to be about 30 s. Thus SO_2 concentration rise begins for both carbons at the beginning of a water flush. For both, the SO_2 emission pattern is irregular and varies from cycle to cycle. There is also a general rising trend in the SO_2 concentrations from cycle to cycle, apparently due to the incomplete removal of H_2SO_4 during a cycle and a slow build-up of acid. This acid reduces O_2 and SO_2 solubilities and thus the rate of SO_2 oxidation.

Most of the SO_2 adsorbed and converted to H_2SO_4 is removed as sulfuric acid duration flushing. However, between flushes, SO_2 continues to be fed to the trickle bed and continues to be oxidized by the O_2 in the simulated stack gas. Acid thus builds up in the carbon particles. Furthermore, the oxidation reaction is exothermic so temperature rises because there is no water flow to remove the heat generated. Because residual liquid is still present in the bed after the water flow is interrupted, the heat released causes evaporation which lowers bed temperature. As the bed temperature falls, the rate of SO_2 oxidation falls as well, and therefore unreacted SO_2 starts to increase in the outlet from

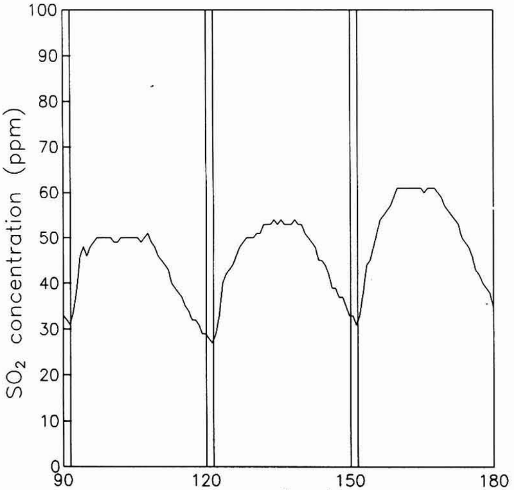

FIGURE 3a Typical SO_2 outlet concentration with Centaur catalyst under periodic operation. Cycle period = 30 min; flush time = 1.5 min; superficial liquid velocity = 0.17 cm/s; temperature of flushing liquid and inlet gas = 80°C.

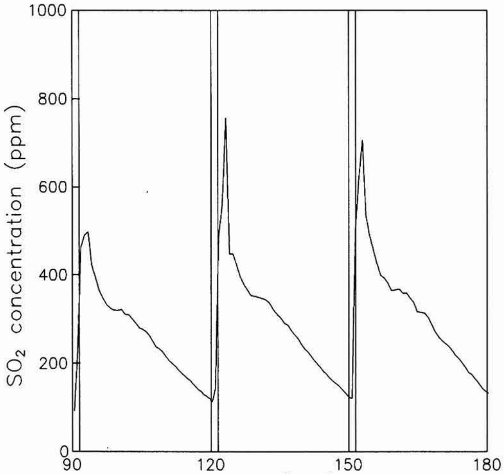

FIGURE 3b Typical SO_2 outlet concentration with BPL catalyst under periodic operation. Cycle period = 30 min; flush time = 1.5 min; superficial liquid velocity = 0.17 cm/s; temperature of flushing liquid and inlet gas = 80°C.

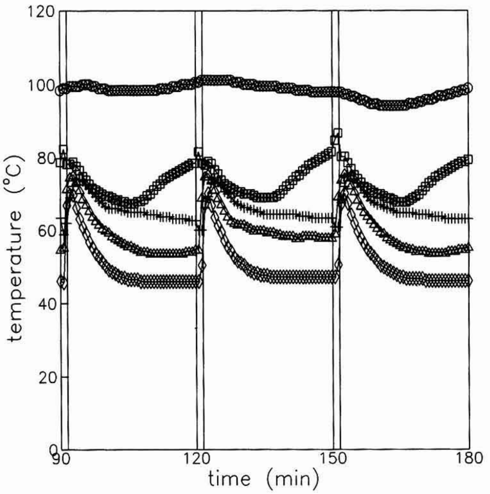

FIGURE 4a Typical temperature profiles of the Centaur catalyst for periodic operation. Conditions as in Figure 3a. ○: top, $r = 0$; □: middle, $r = R$; △: middle, $r = R/2$; ◇: middle, $r = 0$; +: bottom, $r = 0$.

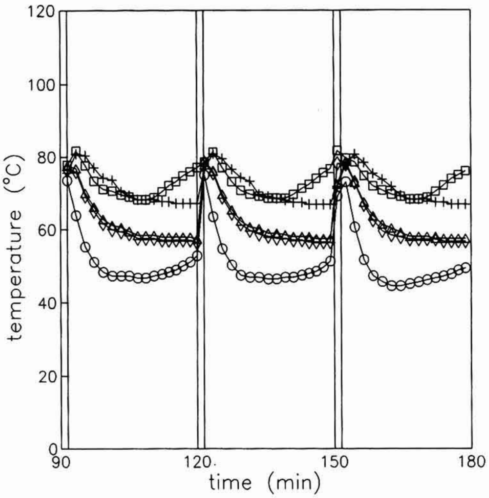

FIGURE 4b Typical temperature profiles of the BPL catalyst for periodic operation. Conditions as in Figure 3b. ○: top, $r = 0$; □: middle, $r = R$; △: middle, $r = R/2$; ◇: middle, $r = 0$; +: bottom, $r = 0$.

the reactor. Once the external liquid hold-up of the bed (i.e., the liquid film and liquid held in interstices between particles) has largely evaporated, the mass transfer resistance drops, enhancing oxygen transfer to the surface and the rate of SO_2 oxidation increases, leading to a decreased concentration in the outlet SO_2. Figures 4a and 4b show the temperature change with time within the bed for the two carbons. Temperature variations are reproducible and seem to correlate well with outlet SO_2 concentration profiles. With the exception of the temperature at the top of the bed (which is the highest temperature for the Centaur carbon and the lowest for BPL), the temperature behavior in both beds is similar—centerline temperatures are lower in the middle of the bed than they are at the bottom and temperatures rise rapidly during flushing, continue to rise for a minute or two after liquid flow is interrupted, and then decline. The decline stops by the middle of the cycle for the upper and middle centerline thermocouples for the BPL carbon and for the middle centerline temperature for the Centaur carbon. The decline does not stop for the bottom thermocouple. Wall thermocouples show increasing temperatures for both carbons. This results from the counter-heating used. The top thermocouple was above the bed for Centaur carbon because of its higher packing density. This thermocouple thus reads only the gas temperature. The top thermocouple is located in the bed for the BPL carbon. Rising temperatures at the end of the cycle for the top thermocouple for both carbons were caused by gas heating and possibly water condensation. Mean bed temperatures are lower for the Centaur carbon, suggesting greater evaporation and higher rates of O_2 transport.

In view of the higher void volume and BET surface area of the BPL carbon and the better performance of the Centaur carbon, these carbons are presumed to have significant differences in their surface characteristics.

Overall Performance under Periodic Flow Interruption

Concentrations of the sulfuric acid leaving the trickle bed reactor are investigated at various splits and periods for the BPL and Centaur catalysts. Performance differences are demonstrated in Figure 5, which shows the effect of split on SO_2 removal for a trickle bed with the BPL and the Centaur catalysts. SO_2 removal is based on the gas analysis and is calculated as follows: $\{1 - y_{SO_2\,\text{outlet}}/y_{SO_2\,\text{inlet}}\} \times$

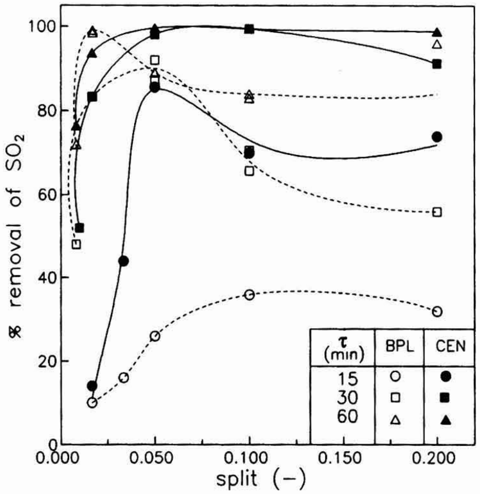

FIGURE 5 Effect of split on SO_2 removal with BPL and Centaur catalysts. Split is the ratio of flushing time to cycle period. Dashed line: BPL catalyst; solid line: Centaur catalyst. Flushing liquid and inlet gas temperature at 80°C.

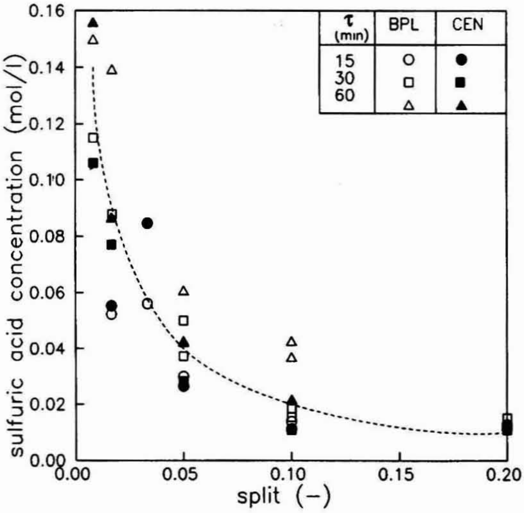

FIGURE 6 Time-average concentration of sulfuric acid leaving the trickle bed at different splits and cycle periods.

100%, where $y_{SO_2\,outlet}$ represents the average outlet value of the mole fraction of SO_2 measured during a cycle. As is evident, the two carbons produced generally the same patterns for SO_2 removal with different split and period, but the % removals are consistently higher for the Centaur material. As the flushing time decreases (i.e., split is reduced), the carbon is not regenerated completely and the SO_2 removal decreases significantly. However, as the flushing time becomes a significant portion of the cycle ($s = 0.2$), the rate of oxygen transfer to the catalyst surface decreases because of an increase in liquid holdup. There appears to be an optimum flushing time which is related to cycle period.

As can be seen in Figure 6, split can be used to raise the concentration of sulfuric acid, though not without causing maldistribution of liquid and poor SO_2 removal performance as a result of incomplete flushing of the catalyst. The increase in sulfuric acid concentration with shorter split was due to an increase in the H_2SO_4 accumulated in the carbon as well as to the smaller amount of flushing liquid used. It can be seen that the type of catalyst has a small effect on sulfuric acid concentration, but the effect of cycle period on sulfuric acid concentration was significant. In the range of those experimental conditions, as the split was decreased twelve-fold, the sulfuric acid concentration leaving the reactor increased fifteen-fold.

Correlation of Scrubbing Performance with DTA Characteristics

Curiously, the performance of the activated carbons is not proportional to the number of oxygen functional groups on their surfaces. Figure 7 shows the DTA curves of the BPL and Centaur carbons. For BPL, there is a sharp rise in the rate of weight loss with temperature between 200°C and 400°C, to a peak followed by a fall, after which there is a slow increase to 700°C. The rate of weight loss then remains constant until 900°C where it again begins to rise more rapidly until about 1250°C, where it remains constant again. The weight loss pattern of the Centaur carbon is quite different from that of the BPL catalyst. There is no peak between 200°C and 400°C. From 500°C to 800°C, there is a gradual increase followed by a faster increase to 1250°C. The weight loss per degree remains higher than the BPL catalyst after 900°C.

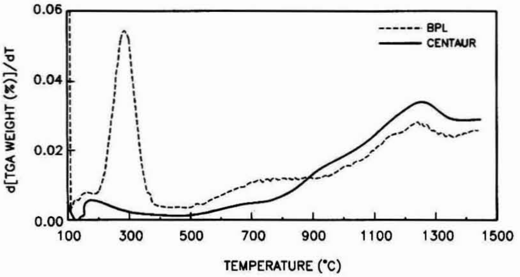

FIGURE 7 DTA curves for BPL and Centaur activated carbon catalysts. Rising temperature range: 100 to 1450°C; heating rate = 10°C/min; flow rate = 120 (STP) mL/min helium over ca. 25 mg sample.

Surface oxygen functional groups are known to decompose as CO and CO_2 at high temperatures in inert atmospheres [7]. Hence, the quantities that are destroyed can be represented indirectly by the temperature-programmed desorption (TPD) analysis. An attempt was made to identify the CO_2 and CO from surface oxygen functional groups of the activated carbons by TPD. As can be seen from Figure 8, the number of oxygen functional groups (CO and CO_2 peaks) for the BPL carbon were greater than those for the Centaur, and CO and CO_2 peak patterns from TPD analysis correspond with the weight loss pattern by DTA. This fact suggests that the oxygen functional groups can be indirectly determined by DTA, which is an even simpler analytical method.

The oxygen functional groups adsorb the SO_2 throughout the oxidation [6]. Therefore, their decrease suggests a

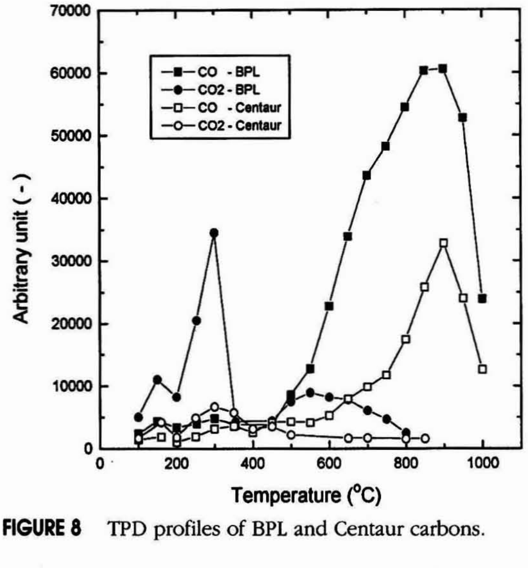

FIGURE 8 TPD profiles of BPL and Centaur carbons.

reduction of adsorption capacity of the activated carbon surface. What then is the explanation of the increase rate of SO_2 oxidation over the Centaur carbon? One possibility is that only some of the oxygen functional groups are capable of promoting the oxidation of SO_2 and that these groups cannot be distinguished by the TPD and DTA techniques used. Another explanation is that there is an optimal density of functional groups. Too high a surface density of oxygen functional groups interferes with the adsorption as a result of the repulsive interaction of SO_2 present in the adsorbed multilayer.

CONCLUSIONS

Catalytic activities of two different activated carbon catalysts for SO_2 oxidation were compared in a periodically operated trickle bed reactor. It was shown that the effect of split on SO_2 removal resulted from the existence of minimum and maximum flushing times. The former arises because a sufficient duration is needed to remove H_2SO_4 from the activated carbon and the latter because liquid flow interferes with the rate of oxygen transfer. For a given period, there is a maximum SO_2 removal that shifts to a higher split as the cycle period decreases. The sulfuric acid concentration increases as split decreases because of the increased accumulation of H_2SO_4 on the carbon catalyst as well as a reduction in flushing liquid.

Catalytic activity of the Centaur catalyst was superior to that of the BPL catalyst in the range of experimental conditions. Results of DTA and TPD experiments were unable to explain the difference in catalytic activity. It was found that surface coverage by the oxygen functional groups for the BPL catalyst was larger than that for Centaur carbon. We hypothesize that the Centaur carbon has a more optimal density of oxygen functional groups.

ACKNOWLEDGMENTS

The financial support of the Natural Sciences and Engineering Research Council in the form of operating grants (to PLS and RRH) is gratefully acknowledged. Dr. J. K. Lee's participation in this project was made possible by a postdoctoral fellowship from Korea Science and Engineering Foundation. Carbons were kindly donated by Calgon Carbon Corporation.

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Oxidation Chemistry of Chloric Acid in NOx/SOx and Air Toxic Metal Removal from Gas Streams

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Chloric acid, $HClO_3$, is a new oxidizer which has recently been shown to be an effective agent in the simultaneous removal of NOx and/or SOx from combustion flue gases and various chemical processes, including nitrations and metal pickling. Aqueous chloric acid readily reacts with NO and SO_2 even in dilute solutions at ambient temperatures. Chlorine dioxide, ClO_2, is formed as a chemical intermediate in the solution phase oxidation reactions. The oxidation by-products of NO include NO_2 and nitric acid. The ClO_2 generated from the solution phase reactions also participates in gas phase oxidation reactions with NO and NO_2. The combined solution phase and fast gas phase reaction chemistries provide the means for creating a new type of high performance NOx/SOx removal process. Wet scrubber based pilot plant tests have demonstrated up to 99% removal of NO.

Additional recent research work has shown that chloric acid is an effective reagent for the removal of air toxic metals, such as elemental mercury, which are present in the waste gas output streams from incinerators, hydrogen from mercury cell chlor-alkali plants, and flue gases of coal-fired power plants. Work in this area is being conducted by Argonne National Laboratories and Olin.

This paper discusses the oxidation chemistry of chloric acid and its unique solution and gas phase reactions with NO, SO_2, and air toxics in wet scrubber type process equipment.

INTRODUCTION

Chloric acid is a new oxidizing agent now being commercially produced by Olin by two electrochemical routes using a sodium chlorate or hypochlorous acid process feedstock. The present major process application for chloric acid is for the generation of chlorine dioxide in pulp bleaching and water treatment. Chlorine dioxide is generated from the reaction of chloric acid with various chemical reducing agents. A distinct environmental and process advantage in using chloric acid is in the control of excess saltcake produced from commercial chlorine dioxide generators. These generators react sodium chlorate with a reducing agent, such as methanol or hydrogen peroxide, in the presence of sulfuric acid which is added to maintain solution acidity. The generator system produces large amounts of sodium sulfate saltcake that often cannot be utilized in the pulping process and which must be discharged or landfilled.

New applications are being developed for chloric acid. These applications are capitalizing on the unique oxidization chemical properties of chloric acid. Chloric acid has a higher oxidation potential than chlorine under most conditions, but is also a very selective oxidizing agent in comparison to chlorine because of one of its main reaction chemical intermediates—chlorine dioxide. The new chloric acid uses described in this paper are for applications in air pollution control technology. These applications include:

- Combined NOx/SOx removal from combustion and chemical process waste gas streams
- Air toxics removal from gas streams such as Hg from coal fired power plants, incinerators, and/or process gases

ELECTROCHEMICAL PROCESSES FOR PRODUCING CHLORIC ACID

Various electrochemical routes for producing chloric acid have been developed by various companies and organizations in the last five years. The main driving force for the initial development of chloric acid has been for the pulp and paper industry, which is increasing chlorine dioxide consumption in pulp bleaching, replacing chlorine as a bleaching agent due to environmental concerns and pending regulations. This increase in chlorine dioxide generation also presents other problems, one of which is sodium imbalance in the mill, resulting in unusable sodium sulfate saltcake which must be disposed or discharged.

These new electrochemical chloric acid processes are based on electrolytic as well as electrodialytic cell designs utilizing two or more cell compartments. Detailed reviews of these electrochemical processes are presented in various papers [*1–7*].

A brief review of Olin's electrochemical routes for producing chloric acid is described in the following section.

SSC® Chloric Acid Process

Olin's SSC® Chloric acid process utilizes a 3-compartment cell design consisting of an anode compartment, central ion exchange compartment, and a cathode compartment. The compartments are separated using cation ion

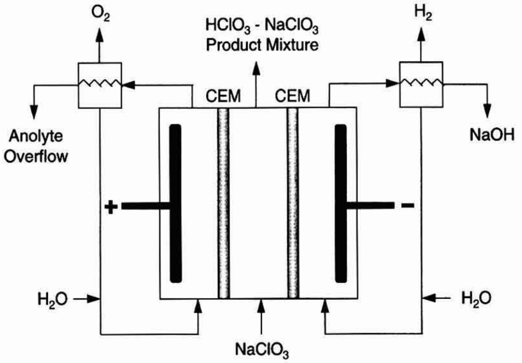

FIGURE 1 SSC® Chloric acid 3-compartment electrochemical process cell operated in a single pass mode configuration.

exchange membranes. Perfluorinated sulfonic acid based cation ion exchange membranes (CEM) are utilized in the cell design due to their oxidation resistance to chloric acid. The process is described in detail in various papers and patents [*1–19*].

Figure 1 shows a typical SSC® Chloric acid 3-compartment electrochemical process cell operating in a single pass mode configuration. Sodium chlorate is passed through the central ion exchange compartment in a single pass producing a chloric acid–sodium chlorate product mixture and co-product NaOH. The catholyte co-product from the process is an aqueous 5–35 wt. % NaOH solution.

Figure 2 shows the SSC® Chloric acid electrochemical process cell operating in a two pass mode configuration. Sodium chlorate is passed through the central ion exchange compartment in a single pass producing a chloric acid–sodium chlorate product mixture which is then introduced into the anolyte circulation loop where the final product is removed. The chloric acid product from this process configuration contains a minor amount of perchloric acid impurity due to partial chloric acid oxidation by the anode. The advantage with this operation configuration is a significant increase in the cell operating current efficiency.

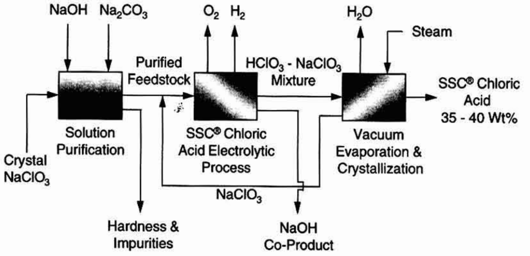

FIGURE 3 SSC® Chloric acid general process flowsheet where a sodium chlorate crystal feedstock is purified to remove hardness and impurities and then fed to the electrochemical process cells.

Figure 3 shows the general process flowsheet for the SSC® Chloric acid process. Commercial sodium chlorate crystal is dissolved and purified to remove trace hardness and metals to insure long life performance of the electrochemical cell membranes. The purified sodium chlorate feedstock is fed to the process cells producing a chloric acid–sodium chlorate product mixture, sodium hydroxide, oxygen, and hydrogen. The chloric acid mixture is then processed in an evaporator/crystallizer under vacuum to remove water from the solution and precipitate sodium chlorate crystals. The final product is a 35–40 wt. % chloric acid solution containing less than 2000 ppm Na^+. The crystallized sodium chlorate from the evaporator is dissolved and recycled back as a feed to the electrochemical cells.

C5 Chloric Acid Process

Olin's C5 Chloric acid process route produces a pure chloric acid product from the direct anodic oxidation of hypochlorous acid, HOCl. The process uses HOCl produced from Olin's commercial J3® Process. A more detailed review of this chloric technology is given in various papers and patents [*1–7, 20–26*].

Figure 4 shows the configuration of the 2-compartment electrochemical cell used in the process. A perfluorinated sulfonic acid cation ion exchange membrane is used to separate the anode and cathode compartments. HOCl is fed into a recirculating anolyte loop producing a chloric acid

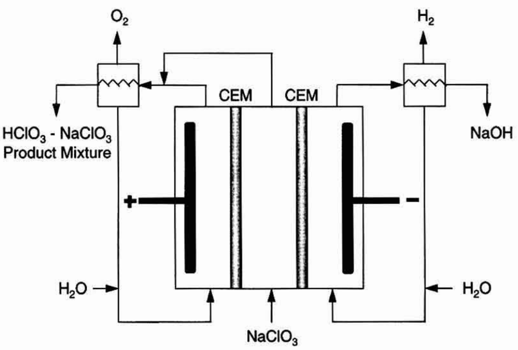

FIGURE 2 SSC® Chloric acid 3-compartment electrochemical process cell operated in a two pass configuration mode to achieve higher current efficiency.

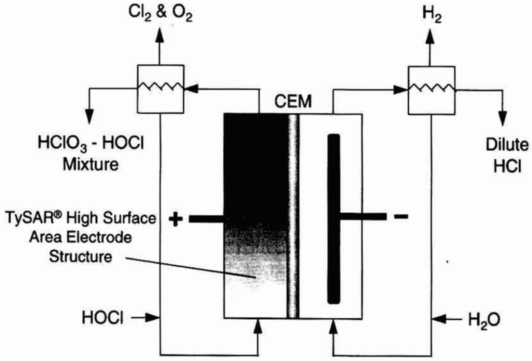

FIGURE 4 C5 Chloric acid electrochemical cell configuration where HOCl is anodically oxidized to chloric acid using a high surface area electrode structure.

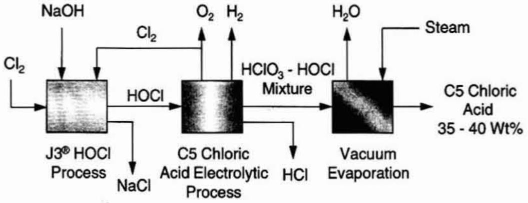

FIGURE 5 C5 Chloric acid general process flowsheet electrochemically converting HOCl into a pure chloric acid solution product.

product solution containing about 18 wt. % chloric acid and 1–3 wt. % residual HOCl. Key to the process is the use of Olin TySAR® IM high surface area anode structures, allowing operation of the electrolyzer at current densities up to 8 kA/m^2 with high anode oxidation selectivity of HOCl to chloric acid.

Figure 5 shows a general flowsheet of the C5 Chloric acid process. Aqueous HOCl solution is fed into the electrochemical process cells and anodically oxidized to chloric acid. The chloric acid–HOCl product mixture is vacuum evaporated to produce a pure chloric acid solution product containing less than 50 ppm Na$^+$.

CHLORIC ACID CHEMICAL PROPERTIES—BRIEF REVIEW

Chloric acid is a strong acid with an acid dissociation constant Ka value of about 500, which is higher than sulfuric acid. About 99% of the chloric acid is ionized at aqueous solution concentrations of about 35 wt. % (about 5.2 molar). Chloric acid is also a strong oxidizing agent, whose oxidizing potential is controlled by the pH of the aqueous solution. The oxidation reaction rates for chloric acid are approximately 2nd order in [H$^+$] concentration [7].

Chloric Acid Oxidation Potentials

Chloric acid is a strong oxidizing agent, whose standard oxidation potential and equivalent weights compare favorably with other chlorine oxidizers as shown by the E^0 standard oxidation potentials given in Table 1.

Chloric acid is a stronger oxidant in acidic media than perchloric acid. Preliminary experiments conducted at Olin have shown that chloric acid has the same capability as perchloric acid for the removal of interferents in pre-treating organic materials for metal analysis. Chloric acid not only has a higher oxidation potential than chlorine or hypochlorite ion under strong acidic conditions, but has the further advantage of having higher aqueous solution concentrations than these other chemical species as well as having a much lower equivalent weight. The oxidation potential of chloric acid is lower than that of chlorine dioxide, but chloric acid has an advantage in stability and higher aqueous concentrations than chlorine dioxide. Chloric acid solutions may be shipped and stored while chlorine dioxide must be produced on-site.

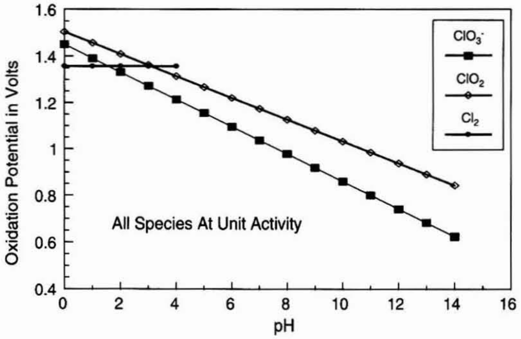

FIGURE 6 Comparison of changes in oxidation potentials for chlorine, chlorine dioxide, and chloric acid versus pH calculated from the Nernst equation for unity activity solutions.

Figure 6 compares the change in oxidation potential for chlorine, chlorine dioxide, and chloric acid as a function of pH calculated from the Nernst equation at unit activities. The data shown is actually very misleading. Chlorine and chlorine dioxide do not exist in aqueous solutions having unit molarity. Use of the Nernst equation,

$$E = E^0 - [0.059/n] \cdot [\log_{10}(a_p/a_r)] \tag{7}$$

where n is the number of electrons and the ratio of activities of the products over the reactants as given in the log term are defined by the appropriate equations as given in Table 1, gives a better picture of oxidation potentials. An example of this is shown in Figure 7, where the oxidation potentials of more realistic concentrations of chlorine and chlorine dioxide are compared to a 1.0 M (8.5 wt. %) solution of chloric acid.

Chloric Acid Shipping & DOT Classifications

Table 2 summarizes the CAS and USDOT (U.S. Department of Transportation) identification and packaging group

TABLE 1. Standard E^0 Oxidation Potentials of Various Chlorine Oxidizers and Their Equivalent Weights in Comparison to Chloric Acid

Oxidizing Agent	Reaction		E^0	Equivalent Weight
$HClO_2$	$HClO_2 + 3H^+ + 4e^- \rightarrow Cl^- + 2H_2O$	(1)	1.584	17.11
ClO_2	$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O$	(2)	1.504	13.49
ClO_3^-	$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$	(3)	1.450	13.91
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	(4)	1.358	35.45
ClO_4^-	$ClO_4^- + 8H^+ + 8e^- \rightarrow Cl^- + 4H_2O$	(5)	1.287	12.43
ClO^-	$ClO^- + 2e^- \rightarrow Cl^- + OH^-$	(6)	0.890	25.72

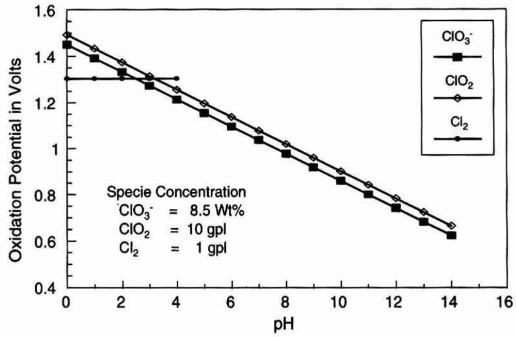

FIGURE 7 Comparison of changes in oxidation potentials for chlorine, chlorine dioxide, and chloric acid versus pH calculated from the Nernst equation for more realistic aqueous solution concentrations as shown.

designations for chloric acid and chloric acid–sodium chlorate mixtures.

NOx/SOx CONTROL/REMOVAL TECHNOLOGY

Numerous methods in the control/removal of NOx and SOx have been developed over the past 20 years. Several technologies are now being used commercially. These NOx/SOx removal methods include the use of various reducing oxidizing agents with/without the assistance of catalysts. A brief summary list of various types of systems and technologies are given below.

- Selective Catalytic Reduction (SCR) based systems utilizing proprietary solid catalysts and added reducing agents such as ammonia or methane.
- Selective Non-Catalytic (SNCR) based systems using area, cyanuric acid, or nitrogen based reducing agents.
- Regenerable sorbent based systems using zeolites, activated carbon or coal, CuO, ZnO, or other materials to adsorb NOx and/or SOx. The sorbents are then regenerated with ammonia, methane, or by other means including heat, microwave, or electron beam energy.

TABLE 2. USDOT Shipping Registration, Identification Numbers, and Packaging Class Assignments for Chloric Acid and Chloric Acid-Sodium Chlorate Mixtures

Item	Chloric Acid	Chloric Acid–Sodium Chlorate Solution Mixtures
Concentration Range	30–40 wt. % $HClO_3$	10–30 wt. % $HClO_3$
CAS Number	7790-93-4 ($HClO_3$)	7790-93-4 ($HClO_3$) 7775-09-9 ($NaClO_3$)
DOT Registration & Classification	Oxidizer 5.1 Pkg. Grp. II Corrosive, Class 8	Oxidizer 5.1 Pkg. Grp. II Corrosive, Class 8
Shipping ID Number	UN 3098	UN3098

- Reducing agent based systems using sulfites or metal chelates such as Ferrous-EDTA.
- Oxidation based systems where NOx and SOx are oxidized to nitric acid and sulfuric acid respectively using various oxidizers including ozone, sodium hypochlorite, peracetic acid, sodium chlorite, chlorine dioxide, and hydrogen peroxide.

SCR and SNCR systems have demonstrated NOx removal efficiencies in the 30–90% range, but are not effective in SOx removal. The new regenerable sorbent based systems have the capability of removing both NOx/SOx. The post processing stages in these regenerable systems are used to desorb the captured chemical species, converting them to nitrogen gas, acids, or other chemical forms such as sulfur. The process performance of the various oxidation and reduction chemical based NOx/SOx removal systems are described in the patent and literature art and will not be detailed here.

CHLORIC ACID BASED NOx/SOx REMOVAL TECHNOLOGY

The Tri-NOx®-NoxSorb® Process is a new wet scrubbing technology capable of simultaneously removing both NOx/SOx from combustion and chemical process waste gas streams based on Olin's NoxSorb® chloric acid based solutions and Tri-Mer Corporation's proprietary process design/equipment [*7, 27–28*].

Figure 8 shows a general schematic of one Tri-NOx®-NoxSorb® Process scrubber configuration employing a NoxSorb® solution oxidation scrubber followed by an alkaline scrubber to remove any residual acid gases. The chloric acid concentration of the NoxSorb® Solution can be tailored to meet the NOx/SOx removal requirements for specific applications. The results of bench scale and pilot test trials in investigating NO (nitric oxide) oxidation/removal is detailed in this paper. More extensive SO_2 and combined NOx/SOx testing is scheduled for this year.

Chloric Acid NOx/SOx Oxidation Chemistry

This section details some of the oxidation reaction chem-

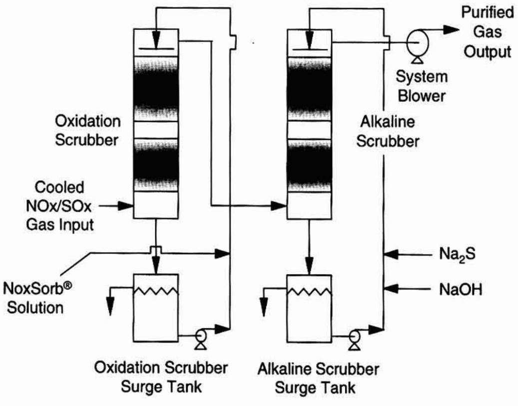

FIGURE 8 General Tri-NOx®-NoxSorb® System wet scrubber tower configuration consisting of an oxidation scrubber followed by an alkaline scrubber having optional sodium sulfide (Na_2S) reducing agent addition.

TABLE 3. Gas Phase and Aqueous Solution Equilibria and Reactions of NO and NO2 in an Oxidizing Environment/ System

Gas Phase		Aqueous Phase	
$2NO + O_2 \rightarrow 2NO_2$	(8)	$N_2O_3 + H_2O \rightarrow 2HNO_2$	(12)
$2NO_2 \leftrightarrow N_2O_4$	(9)	$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$	(13)
$3NO_2 + H_2O \leftrightarrow 2HNO_3 + NO$	(10)	$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$	(14)
$NO + NO_2 \leftrightarrow N_2O_3$	(11)	$3HNO_2 \leftrightarrow HNO_3 + H_2O + 2NO$	(15)

istry of chloric acid and its chemical reaction intermediates with NOx and SOx.

Nitric oxide (NO) is the most difficult NOx gas component to remove in wet scrubber type systems because of its low solubility in aqueous solutions compared to the higher oxidation state gas phase nitrogen-oxygen species which include NO_2, N_2O_3, and N_2O_4. All these gaseous species are in equilibrium and are also in equilibrium with aqueous solution phase species which include nitrous acid, HNO_2, and nitric acid, HNO_3. The gas and solution phase reactions are made even more complex because of additional equilibrium reactions of NO with other gases present, such as oxygen. Table 3 is a summary of the major gas and aqueous phase oxidation and equilibrium reactions of NO [*29*, *30*].

Chloric Acid NOx Oxidation

Chloric acid has been found to react readily with NO even at low chloric acid concentrations at ambient temperature conditions. Chlorine dioxide is formed from the reaction as a reactive chemical intermediate as well as the oxidation by-products of NO, which include NO_2 and nitric acid. Chloride oxide reacts quickly with NO and NO_2 in the gas phase. The properties of the combined solution phase and fast gas phase reactions provide the means for creating a new type of high performance NOx removal process.

The initial reaction of nitric oxide with chloric acid theoretically produces chlorine dioxide and nitrogen dioxide, NO_2, in 1:2 NO:$HClO_3$ molar ratio:

$$NO + 2HClO_3 \rightarrow NO_2 + 2ClO_2 + H_2O \qquad (16)$$

The chlorine dioxide generated in reaction (16) further reacts in gas/liquid phase reactions with both NO and NO_2, producing nitric acid in a series of reactions:

$$\begin{array}{lll} & 5NO + 2ClO_2 + H_2O \rightarrow 2HCl + 5NO_2 & (17) \\ & 5NO_2 + ClO_2 + 3H_2O \rightarrow HCl + 5HNO_3 & (18) \\ \hline \text{Net:} & 5NO + 3ClO_2 + 4H_2O \rightarrow 3HCl + 5HNO_3 & (19) \end{array}$$

If the incoming NO gas reacts with both the $HClO_3$ and the by-product ClO_2 to form only NO_2, then the reaction is the sum of reactions (16) and (17):

$$3NO + HClO_3 \rightarrow HCl + 3NO_2 \qquad (20)$$

Reaction (20) consumes no additional acid, although the by-product HCl generated can further react with chloric acid to produce chlorine and chlorine dioxide:

$$2HClO_3 + 2HCl \rightarrow 2ClO_2 + Cl_2 + 2H_2O \qquad (21)$$

The sum of reactions (16) and (19) gives a net reaction where HCl, HNO_3, and NO_2, are the major process end products:

$$13NO + 6HClO_3 + 5H_2O \rightarrow 6HCl + 3NO_2 + 10HNO_3 \qquad (22)$$

In a wet scrubbing process, the NOx removal efficiency is determined by scrubber system design, control of solution/gas phase temperatures, and by the selection of reactants and their concentrations in the various process stages.

Chloric Acid SOx Oxidation

The initial chemical reactions of chloric acid with SO_2 are theorized to be as follows:

$$\begin{array}{lll} & SO_2 + 2HClO_3 \rightarrow SO_3 + 2ClO_2 + H_2O & (23) \\ & SO_3 + H_2O \rightarrow H_2SO_4 & (24) \\ \hline \text{Net:} & SO_2 + 2HClO_3 \rightarrow H_2SO_4 + 2ClO_2 & (25) \end{array}$$

The by-product ClO_2 produced in net reaction (25) then reacts with additional SO_2 in the gas phase:

$$4SO_2 + 2ClO_2 \rightarrow 4SO_3 + Cl_2 \qquad (26)$$

The chlorine produced in reaction (26) further reacts with water and SO_2 in the gas and liquid phases producing SO_3 and HCl in two reactions:

$$Cl_2 + H_2O \rightarrow HCl + HOCl \qquad (27)$$

$$SO_2 + HOCl \rightarrow SO_3 + HCl \qquad (28)$$

The overall net reaction is the sum of reactions (25–28):

$$6SO_2 + 2HClO_3 + 6H_2O \rightarrow 6H_2SO_4 + 2HCl \qquad (29)$$

Chloric Acid Experimental NO Oxidation Test Results

A series of bench and pilot scale tests were conducted to develop design data on the chemistry and performance characteristics of chloric acid in NO oxidation. The experimental test results are detailed in this section.

Bench Scale NO Oxidation Tests

An initial series of bench scale gas bottle scrubber tests were conducted to determine the effectiveness of NoxSorb® chloric acid solutions in oxidizing NO at ambient temperatures. The test apparatus consisted of 500 ml volume gas impinger scrubbing bottles with coarse frit glass

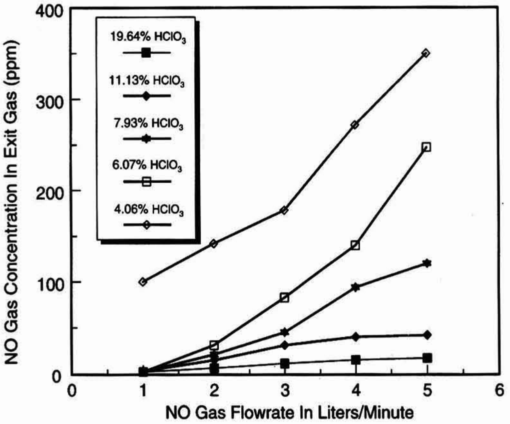

FIGURE 9 Bench scale gas impinger scrubber bottle NO oxidation efficiency test results at ambient temperatures using various chloric acid concentration NoxSorb® Solutions.

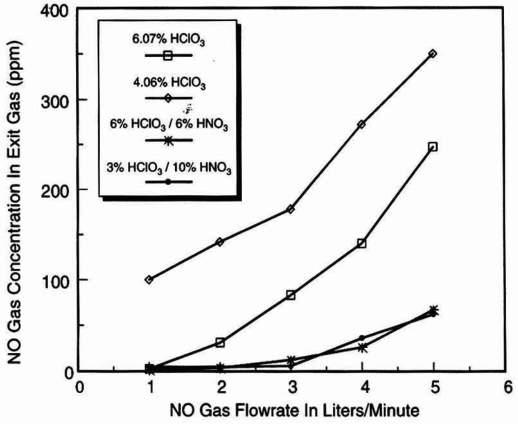

FIGURE 11 Bench scale gas scrubber bottle NO oxidation efficiency test results at ambient temperatures using various chloric acid concentration solutions with nitric acid addition.

gas dispersers filled to 450 ml volumes with various chloric acid concentration solutions. The gas source was NO in argon gas standard obtained from AIRCO which was measured to be 970 ppm NO with a Land Combustion Model 6500 flue gas analyzer. The NO gas was metered into the various scrubber bottles at flowrates ranging from 1–5 liters/min. The outlet NO/NO_2 gas compositions were measured at five selected gas flowrates for each chloric acid solution concentration.

One set of a series of bench scale gas impinger bottle scrubber test results are shown in Figures 9 and 10. Figure 9 shows that the ppm NO concentration in the exit gas decreases with increasing chloric acid solution strength and that the NO exit ppm concentration increases with increasing gas flowrate through the scrubber solution at constant chloric acid solution concentration.

Figure 10 shows the same data set with the percentage of NO oxidation/removal at the various chloric acid solution concentrations and NO gas flowrates. The data shows that chloric acid solution strength is important in achieving high NO oxidation percentages, preferably greater than 90%. The decreasing NO percentage removal at increasing input gas flowrates indicates that the reaction between the chloric acid and NO gas is mass transfer limited in the reaction of the NO gas with the aqueous solution phase in the scrubber bottle. The commercial Tri-NOx®-NoxSorb® Process utilizes a packed bed wet scrubber design to maximize these gas-liquid mass transfer reactions.

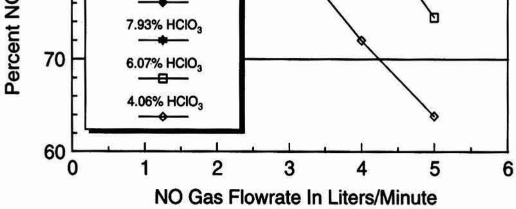

FIGURE 10 Bench scale gas impinger scrubber bottle NO oxidation efficiency test results at ambient temperatures using various chloric acid concentration solutions.

A second series of bench scale gas bottle scrubber tests were conducted to identify whether acid strength was the predominant controlling factor in the NO oxidation reaction and whether the nitric acid reaction by-product would adversely affect the reaction or NO oxidation performance.

Figure 11 shows the test results on the effects of the addition of various amounts of nitric acid to low concentration chloric acid solutions. These results indicate that the hydrogen ion concentration, i.e., acid strength, is a major factor in the reaction chemistry of chloric acid with NO. As was noted in Section 3, chloric acid is a strong oxidizing agent, whose oxidizing potential is controlled by the pH of the aqueous solution where the oxidation reaction rates are approximately 2nd order in $[H^+]$ concentration.

Pilot Plant NO Oxidation Test Results

A series of pilot tests were conducted in a specially constructed 6 inch diameter packed bed scrubber system consisting of a 7 foot packed bed tower, an oxidizer solution recirculation tank and centrifugal pump. A variable speed suction blower was used to control the air flow through the system. Compressed gas cylinders containing 20 wt. % NO gas in nitrogen were used to supply NO into the system air inlet. The NO/NO_2 gas inlet/outlet concentrations were measured using a Land Combustion Model 6500 Flue Gas Analyzer. The NO input concentrations to the oxidation scrubber test system were varied between 1200–2000 ppm by volume.

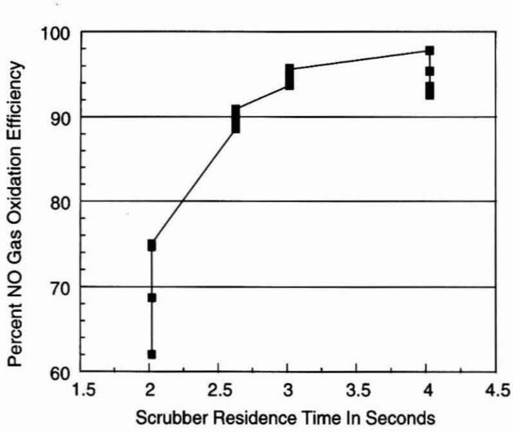

FIGURE 12 Pilot plant chloric acid NO oxidation efficiency performance as a function of scrubber free-air residence time over a wide range of chloric acid concentrations.

Figure 12 shows a summary of a series of fourteen pilot scrubber oxidation performance runs where the percent NO oxidation performance plotted as a function of the scrubber free-air residence time. The scrubber free-air residence times were calculated from the measured air volumetric flowrates passed through the system. Each data point was conducted at various chloric acid concentrations between 10 to 20 wt. % as $HClO_3$. NO oxidation efficiencies of greater than 90% were achieved at scrubber residence times greater than about 2.5 seconds. About 40–60% of the NOx oxidation by-products were captured as nitrate ion (i.e., as nitric acid) in the single stage oxidation scrubber solution.

Additional pilot tests were conducted passing the output gas NO oxidation products from the NoxSorb® oxidation scrubber through an alkaline scrubber in a similar configuration as shown in Figure 8. The exit gas stream from the alkaline scrubber showed less than 6 ppm measured as total NOx, achieving greater than 99% NOx removal.

Figures 13 and 14 show two examples of the NO oxidation performance test data as a function of scrubber free-air residence times of 2.6 and 3.0 seconds respectively at chloric acid concentrations between 15–19 wt. %.

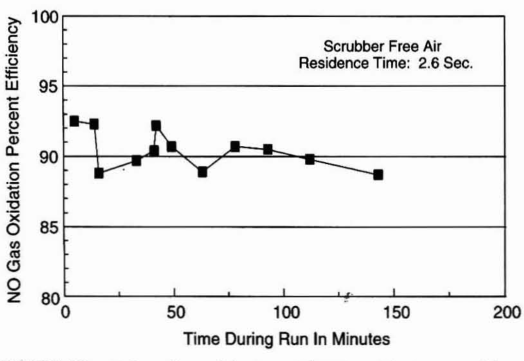

FIGURE 13 Pilot plant chloric acid NO oxidation scrubber efficiency performance at a free-air residence time of 2.6 seconds.

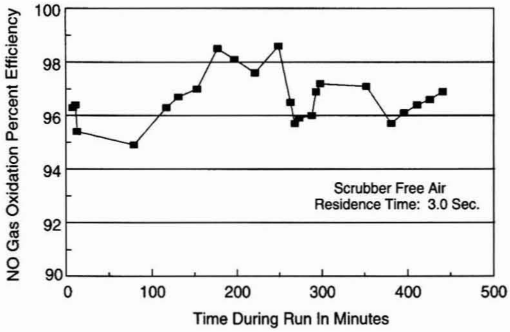

FIGURE 14 Pilot plant chloric acid NO oxidation scrubber efficiency performance at a free-air residence time of 3.0 seconds.

Chloric Acid NOx/SOx Process Applications Summary

The TriNOx®-NoxSorb® Process is especially tolerant to particulates and "dirty" gas input streams because it is a wet scrubber based system. There are no catalysts to poison, inactivate, or give reduced performance with time. The process is suitable for applications in NOx/SOx emission control for incinerators, rotary kilns, direct-fired calciners, internally-fired ovens, stationary diesel generators, as well as for chemical operations such as nitrators and metal finishing processes.

NOx Technology Comparison: NOx Concentration Operating Range

In comparison to the SCR and SNCR NOx removal technologies, the wet scrubber chloric acid based process has the advantage of being able to effectively operate at high removal efficiencies for a wide range of NOx input concentrations. SCR and SNCR technologies have significantly limited NOx operating ranges as seen in the comparison shown in Figure 15.

NOx Technology Comparison: Operating Temperature Range

The process gas temperature is another important factor in NOx process selection. Both the SCR and SNCR systems operate in very limited, high temperature ranges because the chemical and catalyst reaction systems require these

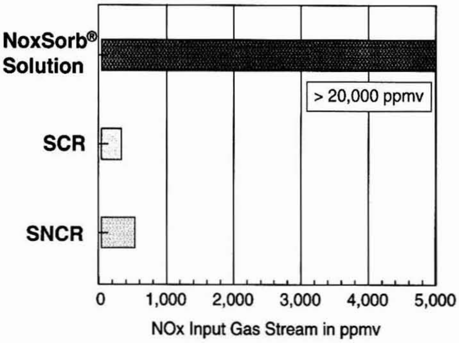

FIGURE 15 Comparison of the NOx input gas concentration operating ranges for the SCR and SNCR NOx removal systems versus the NoxSorb® chloric acid based solution process.

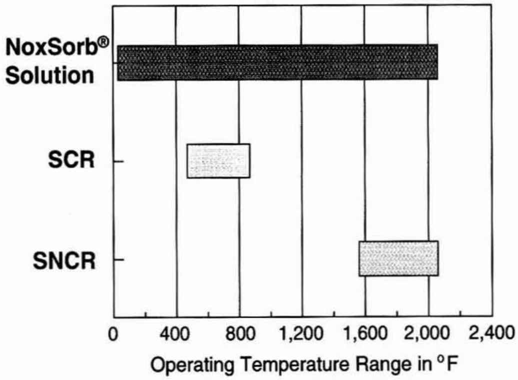

FIGURE 16 Comparison of the operating NOx gas temperature ranges for the SCR and SNCR NOx removal systems versus the NoxSorb® chloric acid based solution process.

high temperatures to effectively function to remove NOx. The Tri-NOx®-NoxSorb® Process uses chloric acid which can operate even at ambient temperatures. Since the process is a wet scrubber based system, the input gas temperatures and process scrubbers can be controlled or modified to operate at any suitable temperature. Figure 16 shows a comparison of the operating temperatures of the SCR, SNCR, and NoxSorb® chloric acid solution based systems.

Potential Retrofit Technology for Coal Fired Plants

In coal fired power plant systems, chloric acid can be potentially employed as a retrofit technology for trimming NOx and SOx emissions. Process designs using NoxSorb® Solution injection into the flue gas stream before or after typical FGD (flue gas desulfurization) stages which use lime or limestone are being investigated. Alternative process schemes are being considered such as ways of potentially recycling a mixed nitric–sulfuric acid product solution from the oxidation stage scrubber.

Chloric Acid in Air Toxics Removal/Control

Title III of the Clean Air Act Amendments of 1990 focused attention on controlling the emissions of various hazardous air pollutants (HAPs). These HAPs, often called air toxics, include metals such as As, Be, Cd, Cr, Pb, Hg, and Se. Mercury and selenium are the most difficult to control, especially from flue gas from combustion processes, because they can remain in vaporized or finely divided elemental form that is difficult to capture. Coal based power plants and incinerators are the major manmade sources of these air toxics.

Flue Gas Elemental Hg Oxidation/Removal

Chloric acid has been recently found to be an extremely effective agent for the oxidation/removal of elemental mercury from simulated flue gas and other process gas streams. Work conducted by researchers at Argonne National Laboratory have shown that chloric acid is the only chemical agent that they have found capable of simultaneous NOx, SOx, and elemental Hg removal in their bench scale simulated flue gas testing [*31–32*].

Gas phase elemental Hg in the 1–20 microgram per m^3 concentration range was reduced to below detectable concentrations using low concentration, i.e., 0.5–1% chloric acid solutions. SO_2 and NO were also simultaneously removed in the tests by 20–40%. The bench scale scrubber system consisted of a glass scrubber body having a single perforated glass plate stage used to distribute a pumped solution down the scrubber column. The system was not optimized for the removal of NOx/SOx.

In addition, some of the data presented by the Argonne researchers indicates that the presence NOx in the gas stream when using chloric acid significantly enhances the oxidation/removal of elemental Hg from the gas stream. A possible reason for this is the gas phase formation of HNO_2 and HNO_3 from the reaction of chloric acid with NOx. The formed nitrous/nitric acid may help to promote the oxidation of the elemental Hg. Nitric acid is commonly used and in combination with HCl in the laboratory protocols for the analysis of mercury compounds and in cleaning laboratory equipment of mercury residues.

Hg Removal from Nitrogen and Hydrogen—Initial Test Results

A series of experiments were conducted investigating elemental Hg removal from hydrogen and nitrogen gas streams using chloric acid. Preliminary test results have shown a 90% or better elemental mercury removal from hydrogen gas streams using a simple series of gas impinger scrubbing bottles filled with aqueous chloric acid.

One set of hydrogen gas stream tests was conducted at hydrogen flowrates of about 3.81 liters/min passed through a series of 250 ml gas impinger scrubber bottles containing various wt. % $HClO_3$ solutions for time periods of about 5–5.5 hours. The mercury removal/collection results are shown in Table 4.

As seen in Table 4, the higher chloric acid concentration solution scrubbers removed/captured mercury more efficiently, in the 90% plus range, while a fivefold diluted solution at 3.98% chloric acid only showed a 57% capture in the first oxidation gas scrubber. It could not be determined from these tests whether the mercury collected in the second and third scrubbers was elemental mercury or oxidized (ionized) mercury that was carried over in the gas stream into the next scrubber(s). The results definitely did show that elemental mercury is oxidized by chloric acid. The chloric acid solution blanks showed between 0.003–0.006 ppm Hg because of the mercury content of the NaOH used to neutralize the solutions before mercury analysis. No interferences were noted in the cold vapor Hg analyzer with the chloric acid solutions. The input hydrogen gas stream Hg concentrations were not constant during each test run because of process source variations.

One experimental test was conducted as a parallel flow collection experiment using a hydrogen gas stream containing elemental mercury and flowing the gas through two parallel scrubber sets. One gas impinger scrubber bottle set was set-up using the EPA potassium permanganate/sulfuric acid mercury collection method consisting of a series of 3 gas impingers each filled with 4 wt. % $KMnO_4$/2.5 wt. % H_2SO_4 solution. The other set of 3 impingers were filled with 9.88 wt. % chloric acid. Hydrogen gas was passed through the scrubbers at a flowrate of 3.81 liters/min for a period of 4.5 hours. The test results are shown in Table 5.

TABLE 4. Elemental Mercury Removal Tests from Hydrogen Gas Using Various Chloric Acid Solution Concentrations in the First Gas Impinger Scrubber followed by Impingers Filled with Potassium Permanganate / Sulfuric Acid Solution

Test #	Scrubber #1 Chloric Acid Solution (wt. %) ppm Hg	Scrubber #2 $KMnO_4/H_2SO_4$ ppm Hg	Scrubber #3 $KMnO_4/H_2SO_4$ ppm Hg	Percent Removal of Hg in Scrubber #1 based on total Hg Collected
1	4.92 ppm (19.88% $HClO_3$)	0.295	0.002	94.3%
2	3.27 ppm (19.88% $HClO_3$)	0.390	0.008	89.1%
3	0.150 ppm (3.98% $HClO_3$)	0.109	0.003	57.3%

A significantly greater amount of mercury was collected in the chloric acid solution scrubber set, indicating that the permanganate/sulfuric acid solution scrubbers may have a limited elemental mercury oxidation/removal capacity if the test results are correct (i.e., there was no equipment contamination).

Mercury removal efficiency in various other tests using chloric acid was found to be a function of chloric acid concentration as well as the method of mass transfer contact with the gas stream. The mercury removal/oxidation mechanism for this system is not known at this time. Additional pilot work is planned using packed wet scrubber equipment to maximize mass transfer and to analyze the scrubber output gas streams to determine the by-products formed from the process.

SUMMARY

Chloric acid, $HClO_3$, is a new oxidizer which has recently been shown to be an effective agent in the simultaneous removal of NOx and/or SOx from combustion flue gases and various chemical processes, including nitrations and metal pickling. Additional research has also shown that chloric acid is an effective reagent for the removal of air toxic metals, such as elemental mercury, which are present in the waste gas output streams from incinerators, hydrogen from mercury cell chlor-alkali plants, and flue gases of coal-fired power plants.

Chloric acid is a strong oxidizer acid that has many potentially useful applications because of its unique oxidation chemistry. Aqueous chloric acid readily reacts with NO and SO_2 even in dilute solutions at ambient temperatures. Chlorine dioxide, ClO_2, is formed as a chemical intermediate in the solution phase oxidation reactions. The oxidation by-products of NO include NO_2 and nitric acid. The ClO_2 generated from the solution phase reactions also participates in gas phase oxidation reactions with NO and NO_2. The combined solution phase and fast gas phase reaction chemistries provide the means for creating a new type of high performance NOx/SOx removal process that has demonstrated up to 99% removal of NO.

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TABLE 5. Metallic Mercury Removal from Hydrogen Gas Tests Conducted using Two Parallel Scrubber Sets*

Scrubber Type Set	Scrubber Solution Composition	Scrubber #1 ppm Hg	Scrubber #2 ppm Hg	Scrubber #3 ppm Hg	Percent Removal of Hg in Scrubber #1 based on total Hg Collected in Scrubber Set 2
$KMnO_4/H_2SO_4$	4 wt. % $KMnO_4$ 2.5 wt. % H_2SO_4	0.076	0.009	0.001	24.1%
Chloric Acid	9.94 wt. % $HClO_3$	0.248	0.057	0.011	78.5%

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*The mercury analysis value are in total ppm Hg collected in each scrubber bottle.

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Adiabatic Thin-Film Evaporation of Volatile Organic Compounds from Industrial Wastewater into a Natural Gas Receiving Stream

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This work develops and presents design parameters for a novel unit operation: adiabatic thin-film evaporation. Liquid flowing downward in a thin film is contacted with gas flowing upward. For applications involving the removal of volatile organic compounds (VOCs) from wastewater, this unit operation is employed and the process design is conducted. In order to prevent cross-media transfer of pollutants, the use of natural gas for the receiving stream is recommended. Subsequent use of the natural gas for fuel would result in destruction of the VOCs. Relative advantages and disadvantages of other technologies for this application are discussed in detail.

INTRODUCTION

The need for technology to remove Volatile Organic Compounds (VOCs) from industrial wastewater has been driven by recent United States Environmental Protection Agency (E.P.A.) regulations; such as, the Benzene National Emission Standards for Hazardous Air Pollutants (NESHAP) Regulation [*2*], the Hazardous Organic NESHAP (HON) Rule [*3*], and the recent standards written by the E.P.A. for treatment of industrial wastewater at Synthetic Organic Chemical Manufacturing Industry (SOCMI) facilities [*1*]. In general, methods for satisfying regulations such as these involve separating relatively low concentrations of organic substances from an aqueous matrix.

Specifically, the Benzene NESHAP Regulation applies to emissions from SOCMI waste streams with benzene levels of 10 ppmw or greater at facilities that process at least 10 Mg/yr of benzene in waste streams. Moreover, the HON Rule is broader in scope, applying to the emissions of 189 hazardous organics from SOCMI wastewater. In general, a SOCMI emission source for Hazardous Air Pollutants (HAPs) subject to the Benzene NESHAP Regulation also would be subject to the HON Rule. Such wastewater also can be generated during the workup of organic reactions occurring in hydrocarbon solvents [*4*].

Wastewater treatment technologies which have been applied to related problems bear significantly upon the problem at hand. Benzene can be removed from industrial wastewater using a variety of stripping methods, such as steam stripping, vacuum stripping, and air stripping [*5*].

Steam stripping involves contacting steam with the wastewater, and can be conducted in a batch or continuous process. Although steam stripping can be quite effective, and theoretically is capable of reducing the concentrations of organics dissolved in wastewater to any desired threshold, it has a major drawback: if the wastewater is not preheated to the temperature of the steam, the process becomes unstable due to sporadic boil-ups. Since most wastewater is significantly cooler than the temperature of saturated steam at ambient pressure, the wastewater would need to be heated prior to steam stripping. This causes the economics of steam stripping to be extremely unfavorable because of the high heat load for preheating.

Vacuum stripping also can be effective, and is capable of removing benzene (or other VOCs) from wastewater to any desired treatment threshold. Vacuum stripping involves reducing the pressure of the vapor over the aqueous phase until benzene and some water vaporize. The vapors are processed in a heat exchanger to condense them, leaving clean water in the liquid phase. Unfortunately, the capital costs associated with vacuum stripping are rather high, since the capital cost of the vacuum pump often can make the process cost-prohibitive.

In a similar vein, air stripping can be efficacious, and can treat wastewater to any desired treatment threshold for benzene. Air stripping involves contacting the wastewater with air, either by bubbling the air into a container of wastewater through the use of a sparger, or by countercurrent flow through a packed absorption column. Unfortunately, air stripping results in transferring contaminants from a wastewater stream into an air stream. In effect, this only transfers the water pollution problem to an air pollution problem. Treatment of the air stream can be conducted by passing it over a bed of activated carbon, but then the air pollution problem will be transformed into a solid waste problem. Thus, air stripping can be considered to provide an incomplete solution to the wastewater problem.

The shortcomings inherent in each of the aforementioned technologies highlight the need for an alternative approach to the problem of removing trace concentrations of volatile organic substances from industrial wastewater.

The differences in volatility between many light hydrocarbons and water suggest evaporation as a potential solution. Evaporation is a well-studied phenomenon, with significant and detailed studies conducted on a number of aspects. Among such work is single-component evaporation from thin films into heated air [*6–11*], and novel methods for designing thin film evaporators [*12–14*], including equipment for such specialty applications as processing temperature-sensitive fluids [*15, 16*]. Other work has examined application of thin-film evaporation in the food industry [*17*], and methods to increase local evaporation rates [*18*].

Thin-film evaporation also has been the subject of extensive studies from a mathematical modeling and kinetic modeling viewpoint [*19–22*]. Most aspects of single-component evaporation, therefore, are well understood.

However, less work has been conducted on the evaporation of multicomponent mixtures. In some of the most directly related work, the isopropanol/water/nitrogen system was studied in detail [*23*]. The kinetics of the evaporation process, and the effects on liquid phase composition, were examined.

Moreover, almost no attention has been given to the design of adiabatic evaporation systems. This is significant because treating a liquid stream with heated gas in order to effect the evaporation process would make system operation cost-prohibitive. The operating costs would be similarly high if the driving force for evaporation was an alternative heat source, i.e., passing a thin film of fluid over a heated plate. Preliminary work on evaporation of organic substances from rivers, streams, and waterfalls has yielded some data regarding rates of volatilization [*24, 25*], but the conclusions of those studies were only that volatile substances will evaporate from water, whereas substances of low volatility have little or no tendency to evaporate.

Work conducted by MacKay and Yeun yielded data on the mass transfer coefficient for evaporation of a variety of organic substances from water [*26*]. The methodology employed a wind-wave tunnel to determine Henry's Law constants and the Schmidt numbers (both for the gas side and the liquid side). The work expressed the mass flux N (mol/m^2 s) of the volatilizing solute as

$$N = K_{OL}(C_W - P/H) \qquad (1)$$

where

$$1/K_{OL} = 1/K_L + RT/HK_G \qquad (2)$$

where K_L, K_G, and K_{OL} are the liquid, gas and overall liquid mass transfer coefficients (m/s), H is the Henry's Law constant (atm m^3/mol), R is the ideal gas constant (82 $*$ 10^{-6} atm m^3/mol K), T is the absolute temperature (K), C_W is the solute concentration in the source liquid phase (mol/m^3), and P is the solute partial pressure (atm). The most crucial parameters are the gas and liquid mass transfer coefficients and the Henry's law constants. Each of these parameters is a function of temperature and pressure, so determination of them must be made at the anticipated operating conditions of equipment to be designed using said parameters. For the purposes of this work, conditions of 293.15 K and 1 atm are used throughout, since those conditions are typical of water requiring treatment for removal of VOCs.

Related work by Harkins, et al. [*27*], developed a mass balance to describe the behavior of gas-liquid contacting operations. The results were of the form

$$c_{effl} = \frac{c_{infl}}{1 + v_g K/v_{infl}} \qquad (3)$$

where c_{infl} is the influent solute concentration in the liquid phase (g/L), c_{effl} is the effluent solute concentration in the liquid phase (g/L), v_g is the gas flowrate (L/min), K is the Henry's law constant for the solute (dimensionless), and v_{infl} is the influent liquid flow rate (L/min). The theoretical development does not depend on the use of any particular gas species for the removal of refractory organics from a liquid phase. Thus, while Harkins, *et al.* [*27*] applies equation (3) only to systems where water is the source phase and air is the receiving phase, any gas species could be used in the proportions predicted by equation (3). The significance of this will be discussed later (*vide infra*).

The work by MacKay and Yeun [*26*], combined with the related work by Harkins, *et al.* [*27*], on gas-liquid contacting operations for the removal of volatile impurities from liquid phases, provide the basis for the design of a novel unit operation for treatment of industrial wastewater contaminated with volatile impurities.

The specific example considered in this work is the removal of benzene from an industrial wastewater stream for compliance with the Benzene NESHAP Regulation [*2*]. In a typical case, wastewater saturated with benzene at 1800 ppmw (1.8 g/L) [*28*] is treated in an enclosed system until the benzene level is 10 ppmw (0.01 g/L), at which point the wastewater can be discharged to an open biotreatment system. For the purposes of this work, it is assumed that no other impurities exist in the wastewater.

ADIABATIC THIN-FILM EVAPORATION INTO A NATURAL GAS RECEIVING PHASE

Consider a falling film of liquid in contact with gas forced upward, as shown in Figure 1. In order to design a system to transfer impurities from the liquid phase to the gas phase, two main parameters must be determined: the surface area required for mass transfer, and the vapor:liquid ratio. The mass transfer constants determined by MacKay and Yuen [*26*] can be employed to determine the surface area re-

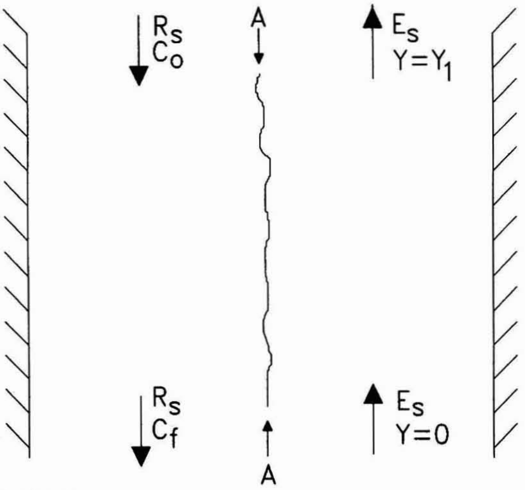

FIGURE 1 Thin-film evaporation process.

TABLE 1. Equilibrium Concentrations and Mole Ratios in the Benzene / Water / Inert Vapor Ternary System

c_1 (ppm)	c_1 (g/L)	c_g (g/L)	x	y^*	X	Y^*	Y^*/X
0	0	0	0	0	0	0	276.1‡
300	0.3	0.0666	0.00007	0.01913	0.0007	0.01951	281.5
600	0.6	0.1332	0.00014	0.03827	0.00014	0.39792	287.1
900	0.9	0.1998	0.00021	0.05740	0.00021	0.06090	292.9
1200	1.2	0.2664	0.00028	0.07654	0.00028	0.08288	298.9
1500	1.5	0.3330	0.00035	0.09567	0.00035	0.10580	305.2
1800	1.8	0.3996	0.00042	0.11481	0.00042	0.12970	311.8

‡Limiting ratio for exceedingly low benzene concentrations, calculated at 0.01 ppm.

quired for mass transfer, and the work by Harkins, *et al.* [27] can serve as a limiting case, since their development represents the case where equilibrium is reached between the vapor and liquid phases. It is assumed that benzene is the only transferred component, i.e., the water and gas act as inerts. It is recognized that a finite amount of water will vaporize, but the quantity of water vaporized is the subject of previous work [5]. Specifically, the assumption of water as an inert assists the theoretical development because it allows changes in liquid concentrations due to evaporation of water to be ignored. In this respect, the assumption certainly is reasonable.

Using the notation and units of Harkins, *et al.* [27] Henry's law can be expressed as

$$c_g = Kc_1 \tag{4}$$

where c_g is the concentration in the gas phase (g/L). A Henry's law constant of 0.222 was used [27]. The equilibrium data so obtained are converted to the mole fractions x and y for the liquid and vapor phases, respectively. (The unit conversions for the vapor phase do not depend on data pertaining to any particular gas species, only that the gas behaves ideally. Thus, the derivation is valid for any gas species displaying ideal or near-ideal behavior). This allows conversion to the mole ratios

$$X = \frac{x}{1-x} \tag{5}$$

and

$$Y = \frac{y}{1-y} \tag{6}$$

where the mole ratios X and Y represent mole of benzene per mole of non-benzene in the liquid and vapor phases, respectively. The equilibrium mole fractions y^* can be expressed as

$$y^* = K'x \tag{7}$$

where K' is a modified Henry's law constant which accounts for unit conversions from concentrations in g/L to mole fractions. However, it cannot be stated that

$$Y^* = K'X \tag{8}$$

because

$$Y^* = \frac{y^*}{1-y^*} = \frac{K'x}{1-K'x} \tag{9}$$

Thus, on an X-Y plot, the equilibrium curve is not expected to be straight over the entire domain of possible X values. As indicated in Table 1, for the compositions of interest in the application at hand, the equilibrium data will show a slight curve. The parameter Y^*/X increases from 276.1 at near-zero concentrations to 311.8 at a liquid composition of 1800 ppm benzene.

The X-Y plot is shown in Figures 2 and 3. Figure 2 highlights the top portion of the evaporator, while Figure 3 is expanded to highlight the bottom portion of the unit. Point "a" (Figure 3) represents the specified liquid effluent of 10 ppm, which is contacted with a vapor stream containing no

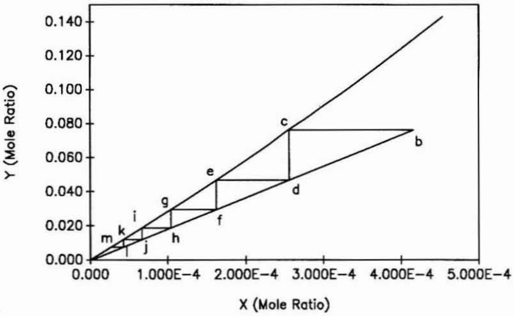

FIGURE 2 Equilibrium and mass balance data for upper portion of evaporator.

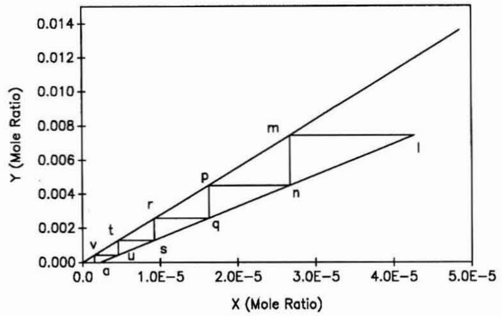

FIGURE 3 Equilibrium and mass balance data for lower portion of evaporator.

benzene. Figures 2 and 3 also yield the minimum vapor:liquid ratio required to achieve the specified evaporation of benzene from the liquid phase. The equation of the operating line is

$$G_s(Y_1 - Y) = L_s(X_1 - X) \tag{10}$$

where G_s is the mass flux of the gas, on a benzene free basis, and L_s is the mass flux of the liquid, again on a benzene free basis. The point (X_1, Y_1) can be any known point on the operating line. In the case at hand this point corresponds to the conditions at the bottom of the evaporation unit, where liquid must exit at a benzene level of no greater than 100 ppmw ($X = 2.31 * 10^{-6}$) and gas is assumed to enter the unit with no benzene content ($Y = 0$).

The operating line is line "lb" in Figure 2, and line "al" in Figure 3 (overall, line "ab" in both figures). The slope of the equilibrium curve at the bottom of the unit approximates the maximum liquid:vapor ratio which can achieve the separation process. (Since point "a" in Figure 3 is so close to the origin, this approximation is used in order to prevent the size of the unit from becoming unmanageable. In strict terms, the maximum liquid:vapor ratio is that which corresponds to the operating line drawn tangent to the equilibrium curve, with an infinite number of equilibrium stages.) If a 50% excess of gas is specified, the slope of the operating line is set at two-thirds of the slope of the equilibrium curve at the origin, and the operating line is completely specified. For a basis liquid flow rate of 1.0 mol/s, the gas flow rate would be 0.005433 mol/s. Again, this could be for any gas. The significance of being able to vary the gas species will be considered later (*vide infra*, Discussion Section).

The evaporator can be designed by comparing equilibrium data with the equation for the operating line, in a stepwise process. The procedure is shown graphically in Figures 2 and 3. Starting at the top of the unit, equilibrium stages can be represented by steps taken between the operating line and the equilibrium curve. For the upper portion of the evaporator, this is shown on Figure 2 as path "bcdefghijklm." Similarly, for the lower portion of the evaporator, the process is shown on Figure 3 as path "lmnpqrstuv." Point "v" represents a benzene level in the effluent less than the 10 ppmw regulatory threshold (point "a"). Altogether, 10 equilibrium stages are calculated.

The surface area required for mass transfer can be obtained by using the data reported by MacKay and Yeun [26]. The overall mass transfer coefficients for evaporation of benzene as a function of vapor velocity are displayed in Table 2.

This suggests that there are a range of possible design operating conditions. Consider a multiple-plate falling-film evaporator, with several plates of the variety shown in Figure 1 in parallel. Table 2 implies that, for a fixed gas flux and fixed liquid film thickness, the velocity can be varied by narrowing or widening the distance between the plates.

TABLE 2. Mass Transfer Coefficients for Benzene [26]

Vapor Velocity (m/s)	5.96	7.09	8.57	10.31	11.67	13.2
K_{OL} (10^6 m/s)	30.0	39.0	51.8	68.4	82.4	99.1

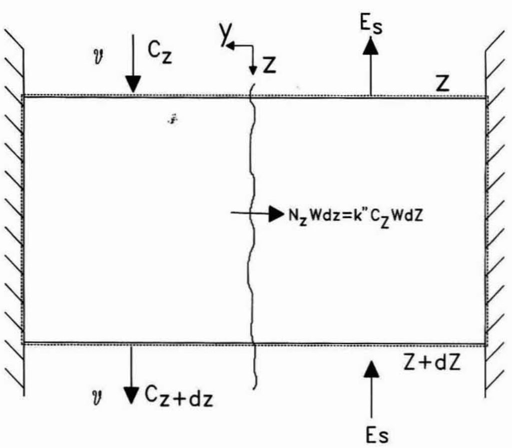

FIGURE 4 Differential element of thin-film evaporator.

Consider a differential element of the thin-film evaporation unit of thickness *dz*, as detailed in Figure 4. A mass balance on benzene for the liquid side of the element, denoted by the dashed line, is

$$\text{In} - \text{Out} = \text{Accumulation} \tag{11}$$

For steady state operation, there is no accumulation, so the mass balance becomes

$$\begin{array}{ccc} \mathcal{V} c_z - & [\mathcal{V} c_{z+dz} + N_z W dz] & = 0 \\ \text{In} & \text{Out} & = 0 \end{array} \tag{12}$$

where $\mathcal{V}$ is the volumetric flow rate of liquid in the film (assumed constant), c_z is the concentration of benzene in the liquid entering the differential element, c_{z+dz} is the concentration of benzene in the liquid leaving the differential element, N_z is the mass flux of benzene from the liquid to the vapor phase at the differential element, and W is the width of the film. Rearranging equation 12 yields

$$c_{z+dz} - c_z = \frac{-N_z W dz}{\mathcal{V}} \tag{13}$$

or

$$\frac{dc}{dz} = \frac{-N_z W}{\mathcal{V}} \tag{14}$$

An expression for the mass flux of benzene at position z can be obtained from equation 1 by employing Raoult's law, i.e.,

$$\begin{aligned} N = K_{OL}(c - P^*/H) &= K_{OL}(c - P^v x/H) \\ &= K_{OL}c(1 - k' P^v/H) = k'' c \end{aligned} \tag{15}$$

where P^* is the partial pressure of benzene in the vapor phase, P^v is the vapor pressure of benzene, k' is a conversion factor to account for the ratio between concentration and mole fraction, and

$$k'' = K_{OL}(1 - k' P^v/H) \qquad (16)$$

This permits rearrangement of equation 14 to

$$\frac{dc}{c} = \frac{-k'' W}{\mathcal{V}} dz \qquad (17)$$

which, when integrated from conditions of $c = c_o$ at $z = 0$, yields

$$c = c_o \exp(-k'' Wz/\mathcal{V}) \qquad (18)$$

This allows complete design of a thin-film evaporation system for an application such as the removal of benzene from industrial wastewater. Of the parameters in equation 18, k'' can be determined from the data reported by MacKay and Yeun [*26*], while W and $\mathcal{V}$ can be selected as design variables. In other terms, if a design required the length of the falling film z, and the parameters c_f, c_o, W, k'', and $\mathcal{V}$ are specified, then

$$z = (\mathcal{V}/k'' W) \ln(c_o/c_f) \qquad (19)$$

where c_f is the final concentration of pollutants desired in the wastewater (in this case, 10 ppmw for benzene in the wastewater effluent). Perhaps even more useful is the form

$$A = (\mathcal{V}/k'') \ln(c_o/c_f) \qquad (20)$$

where A is the total surface area required for the evaporations process.

As an example, consider a basis liquid flow rate of 1.0 mol/s, with an influent benzene level of 1800 ppm. As stated previously (*vide supra*), the Benzene NESHAP Regulation would mandate treatment to reduce the benzene level to 10 ppm. From Table 2, a value of K_{OL} of 30.0×10^{-6} m/s is obtained. (The most conservative value was selected from Table 2 in order to ensure that the system is not underdesigned. In order for the value of K_{OL} to be valid, the spacing between plates must be calculated in order to maintain a gas velocity at least that specified in Table 2.) A liquid volumetric flow rate $\mathcal{V}$ of 1.80×10^{-5} m^3/s is obtained, and the conversion factor k' is calculated to be 1.8×10^{-5} m^3/mole. The Henry's law constant H of 4.39×10^{-3} atm m^3/mole was used [*26*], and the vapor pressure P^v of 0.1 atm was employed [*26*]. This yielded a value of k'' of 2.9988×10^{-5} m/s, and resulted in an area (per Equation 20) of 3.12 m^2.

DISCUSSION

The choice of receiving gas merits additional attention. The design did not depend on any particular gas being used as the receiving stream. Air might be the most logical choice for a receiving stream, simply because it has no cost. However, such an approach certainly would be shortsighted, and only would result in cross-media transfer of pollutants. A multimedia approach to pollution prevention suggests that using natural gas as the receiving stream offers some distinct advantages [*29*]. Natural gas ultimately is used for fuel, so any pollutants dissolved in the natural gas would be destroyed in the combustion process. In contrast, treatment of the air likely would be accomplished by passing the air across a bed of activated carbon. Thus, the water pollution problem first is converted to an air pollution problem and then to a solid waste problem. Accordingly, it is recommended that natural gas be used as the receiving stream for the thin-film evaporation process. It is assumed that all of the natural gas for this thin-film evaporation process is used on site, and that there are no permitting issues involved. The combustion products may need to be monitored, especially if the combusted mixture contains sulfur, halogens, or other heteroatoms.

A typical design for an industrial-scale system to remove benzene from wastewater at the aforementioned inlet and outlet concentrations can assume a basis wastewater flow rate of 3785 liters/min (1000 GP.). Using the design method presented herein, a gas flow rate of 26.9 standard cubic meters per minute (950 SCFM) would be required, and the minimum area for evaporation would be $1.09 * 10^4$ m^2.

CONCLUSIONS

This work has developed a novel unit operation: adiabatic thin-film evaporation, and has applied the unit operation to the problem of removing volatile substances from industrial wastewaters. If natural gas is used as the receiving stream, then a permanent solution to the pollution problem can be attained.

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Modelling VOC Emissions at Wastewater Drop Structures

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A mechanistic model was developed to predict VOC emissions at drop structures. The mass transfer mechanisms that have been incorporated into the model include the falling film (disintegrating jet), turbulent mixing in the area of jet impact, and bubbles in the tailwater resulting from air entrainment. Air entrainment appears to be the most significant mechanism affecting VOC emissions, following by the falling film. A sensitivity analysis was also performed using parameter values that are considered "typical" for wastewater drop structures and operating conditions. The largest variation in stripping was associated with air entrainment, liquid and air flow, Henry's law coefficient and degree of equilibrium for entrained bubbles.

INTRODUCTION

In North America, significant attention has been given to the emission of volatile organic compounds (VOCs) from wastewater. This attention stems from several concerns, including contribution of VOCs to the formation of photochemical oxidants and the risk of human exposure to potentially toxic VOCs. Various regulations have been passed to reduce and eliminate VOC emissions, e.g., Titles 3 and 8 of the U.S. Clean Air Act of 1990, AB2588 in California.

To address the concerns identified by the regulations, the Water Environment Research Foundation sponsored a critical review of the literature describing the transport and fate of VOCs in wastewater collection systems [*4*]. The review reveals a lack of understanding of the mechanisms contributing to the stripping of VOCs within collection and treatment systems. Without proper understanding, it is difficult to identify locations with high VOC emissions and to subsequently design modifications which can be used to reduce VOC emissions from such systems. These systems include hydraulic structures such as clarifier weirs and drops into wet wells.

Currently, oxygen transfer models are the basis for prediction of VOC transfer at drop structures [*6, 16*]. However, the usefulness of oxygen transfer models for estimating VOC stripping is limited by the highly empirical nature of such models. Furthermore, the mass transfer mechanisms that most influence oxygen transfer may not be consistent with those that most influence VOC stripping. To assess the relative importance of the various mechanisms involved, a mechanistic model was developed to calculate VOC stripping at hydraulic drop structures. This paper describes the development of the model and the modelling results.

MECHANISTIC MODEL

The mechanistic model is based on the conservation of mass and on the principles of mass transfer. The governing control volume is depicted in Figure 1, which shows a generic drop structure and identifies the five distinct mechanisms that have been considered in the model. The mass transfer pathways are: 1) from the falling film, 2) from the disintegrating droplets, 3) from the splashing droplets, 4) from the tailwater surface, and 5) to the bubbles in the tailwater resulting from air entrainment.

The following assumptions have been incorporated into the model which describes steady state emissions from a generic drop structure: 1) chemical and biological reactions have been neglected, 2) sorption to suspended solids has been neglected, 3) the tailwater pool is treated as a continuous stirred tank reactor (CSTR), 4) the air in the headspace is treated as a CSTR, 5) the falling water is treated as a plug flow reactor (PFR), and 6) the individual droplets or air bubbles created are treated as batch reactors.

Each mechanism incorporated into the model is referred to as a separate "Term." For the development of each term, the rate of gas-liquid mass transfer between wastewater and the atmosphere is expressed as:

$$E_v = K_L A\left(C_w - \frac{C_g}{H_c}\right) \tag{1}$$

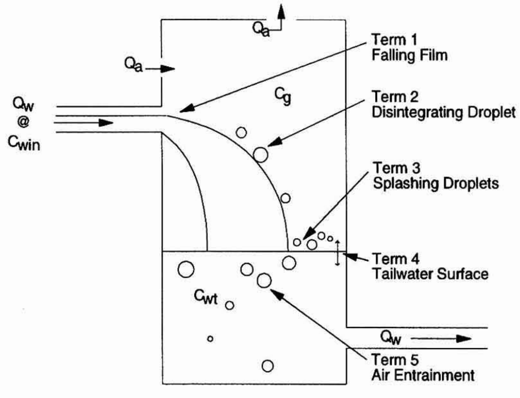

FIGURE 1 Transfer mechanisms considered in model.

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where E_v = rate of mass transfer across water-air interface (g/s)
K_L = overall liquid phase mass transfer coefficient (m/s)
A = area of water-air interface (m^2)
C_w = concentration of contaminant in the liquid phase (g/m^3)
C_g = concentration of contaminant in the gas phase (g/m^3)
H_c = compound-specific Henry's Law constant $[(g/m^3)_{gas}]/[(g/m^3)_{liq}]$

The overall mass transfer coefficient is frequently unknown or unquantified, particularly with respect to an individual mechanism in an overall process. In many applications, including that considered here, it is difficult to estimate a value or judge whether a specific number is of the correct order of magnitude. Nevertheless, if equilibrium is achieved, conservation of mass does limit the total transfer rate to the hydraulic flow times the difference between the inlet concentration and the outlet concentration. With recognition of this limit, it is possible to rewrite Eq. 1 as,

$$E_v = Q_w \gamma_i \left(C_w - \frac{C_g}{H_c} \right) \tag{2}$$

where Q_w = wastewater flowrate (m^3/s)
γ_i = degree of equilibrium achieved (−)

A degree of equilibrium factor, γ_i, is inserted to account for the general case in which the maximum possible transfer is not achieved. At first look, it would appear that one unknown parameter has been replaced by another unknown parameter. However, while the mass transfer coefficient can vary anywhere from zero to infinity, the degree of equilibrium is limited to the range 0 to 1. In systems where knowledge is limited, this more restricted range may be easier to work with and interpret physically. Ultimately, the degree of equilibrium factor and the mass transfer coefficient are related to one another. The specific relationship is dependent on whether the setting is a batch, plug flow or continuous stirred tank reactor and can be derived from setting Eqs. 1 and 2 equal. Table 1 provides the relationship between the degree of equilibrium and the mass transfer coefficient for each of the mechanisms included in the model.

Falling Film

Term 1 accounts for mass transfer at the surface of the falling film of water entering the drop structure. Emissions are estimated as,

$$E_{film} = Q_w \gamma_{ff} \left(C_{win} - \frac{C_g}{H_c} \right) \tag{3}$$

where γ_{ff} = degree of equilibrium achieved during water fall
C_{win} = contaminant concentration in the influent water (g/m^3)

TABLE 1. Degree of Equilibrium—Mass Transfer Coefficient Relationships

Degree of Equilibrium (γ)	Reactor Type (Batch, PFR, CSTR)	$\gamma = f(K)$
γ_{ff}	PFR	$1 - \exp(-K_{ff} A_{ff}/Q_w)$
γ_{dd}	Batch	$1 - \exp(-K_{dd} A_{dd}/Q_{dd})$
γ_{sd}	Batch	$1 - \exp(-K_{sd} A_{sd}/Q_{sd})$
γ_{surf}	CSTR	$K_{surf} A_{surf}/Q_w$
γ_e	Batch	$1 - \exp(-K_e A_e/Q_e)$

Disintegrating Droplets

Term 2 represents emissions from droplets formed by the disintegrating waterfall. The extent of disintegration can range from negligible to complete and is a function of drop height, hydraulic flow and nappe thickness. The droplets formed at different heights of the waterfall will have different contaminant concentrations since concentration varies with height. However, it is assumed that the droplet concentration upon generation is equal to the influent water concentration (C_{win}). Emission contributions from Term 2 are given by,

$$E_{disintegration} = Q_{dd} \gamma_{dd} \left(C_{win} - \frac{C_g}{H_c} \right) \tag{4}$$

where Q_{dd} = flowrate of disintegration droplets generated (m^3/s)
γ_{dd} = degree of equilibrium achieved by the disintegrating droplets

Splashing Droplets

Term 3 represents emissions from droplets created by splashing at the tailwater surface. The degree of splashing is a function of flowrate and slope of the waterfall impingement. Initially, these droplets will have the concentration of the tailwater. A single area and mass transfer coefficient is assumed to apply for all droplets. Emissions due to splashing may be expressed as,

$$E_{splashing} = Q_{sd} \gamma_{sd} \left(C_{wt} - \frac{C_g}{H_c} \right) \tag{5}$$

where Q_{sd} = flowrate of splashing droplets generated (m^3/s)
γ_{sd} = degree of equilibrium achieved by the splashing droplets
C_{wt} = contaminant concentration in the tailwater (g/m^3)

Tailwater Surface

Term 4 accounts for emissions from the tailwater surface and may be described by the general mass transfer rate equation,

$$E_{surface} = Q_w \gamma_{surf} \left(C_{wt} - \frac{C_g}{H_c} \right) \tag{6}$$

where γ_{surf} = degree of equilibrium achieved for tailwater.

Air Entrainment

Term 5 represents emissions resulting from mass transfer between the tailwater and entrained air. It has been assumed that the initial concentration in the bubble is equal to the headspace concentration. The bubble is assumed to behave as a batch reactor during its travel through the tailwater and as such the emissions can be determined by

$$E_{\text{entrainment}} = Q_e \gamma_e \left(H_c C_{wt} - C_g \right) \qquad (7)$$

where Q_e = rate of air entrainment (m^3/s)
γ_e = degree of saturation of the entrained air bubbles prior to resurfacing

Total Emissions

The estimated total emissions, E (g/s), for the drop structure is the sum of the contributions from the five identified mass transfer mechanisms in Eqs. 3 to 7:

$$\text{Total } E = E_{\text{film}} + E_{\text{disintegrating}} + E_{\text{splashing}} + E_{\text{surface}} + E_{\text{entrainment}} \qquad (8)$$

Combining like terms, E becomes:

$$E = \left(Q_w \gamma_1 + Q_{dd} \gamma_{dd} \right) \left(C_{\text{win}} - \frac{C_g}{H_c} \right) + \left(Q_{sd} \gamma_{sd} + Q_w \gamma_{\text{surf}} + H_c Q_e \gamma_e \right) \left(C_{wt} - \frac{C_g}{H_c} \right) \qquad (9)$$

Since emissions, tailwater concentration, and headspace concentration are not mutually independent, they need to be linked by the conservation of mass. Under steady state conditions, the tailwater concentration can be related to emissions by

$$E = Q_w \left(C_{\text{win}} - C_{wt} \right) \qquad (10)$$

while for the headspace,

$$E = C_g Q_a \qquad (11)$$

where Q_a = gas flowrate out of drop structure headspace (m^3/s)

Combining Eq. 9 with Eqs. 10 and 11, and assuming that the incoming air contains no contaminant, the emissions equation becomes:

$$E = \frac{C_{\text{win}} \left(Q_w \gamma_1 + Q_{dd} \gamma_{dd} + Q_{sd} \gamma_{sd} + Q_w \gamma_{\text{surf}} + Q_e \gamma_e H_c \right)}{\left[1 + \frac{\left(Q_w \gamma_1 + Q_{dd} \gamma_{dd} + Q_{sd} \gamma_{sd} + Q_e \gamma_e H_c \right)}{Q_a H_c} + \frac{\left(Q_{sd} \gamma_{sd} + Q_w \gamma_{\text{surf}} + Q_e \gamma_e H_c \right)}{Q_w} \right]} \qquad (12)$$

The emissions could also be calculated as a percentage of the influent compound, using:

$$\% \text{volatilized} = \left(1 - \frac{C_{wt}}{C_{\text{win}}} \right) \times 100 \qquad (13)$$

TABLE 2. Parameter Values

Variable (units)	Typical Value	Minimum Value	Maximum Value
H_c ($m^3_{\text{liq}}/m^3_{\text{gas}}$)	0.5	0.1	2.5
C_{win} (mg/m^3)	200	10	3000
Q_w (m^3/s)	0.15	0.003	0.613
Q_a (m^3/s)	10^{20}	0.0025	10^{20}
Q_e (m^3/s)	$10\ Q_w$	$1\ Q_w$	$30\ Q_w$
$Q_{dd}\gamma_{dd}$ (m^3/s)	$0.005\ Q_w$	$10^{-5}\ Q_w$	$0.3\ Q_w$
$Q_{sd}\gamma_{sd}$ (m^3/s)	$0.005\ Q_w$	$10^{-5}\ Q_w$	$0.3\ Q_w$
γ_{ff} (−)	0.05	10^{-5}	0.5
γ_e (−)	0.5	0.1	1.0
γ_{surf} (−)	0.005	10^{-5}	0.3

PARAMETER ESTIMATION

Calculation of the emissions from a particular drop structure requires values for the 12 parameters in Eq. 12. These 12 parameters are reduced to 10 in the analysis here by coupling the flow and degree of equilibrium for the disintegrating droplets and splashing droplets. Table 2 gives typical, minimum, and maximum values used to test the model's behavior. These values are based on findings in the literature. Where necessary, estimates were made. In some cases, these estimates were arbitrary. The basis for selecting the various parameter values follows.

Henry's Law Coefficient, H_c

The typical value and extremes were selected based on VOCs that are commonly observed in municipal wastewater. At 20°C, a lower-band of $H_c = 0.1$ corresponds to VOCs such as dichloromethane, while extremely highly volatile compounds correspond to H_c of approximately 2.5. The "typical" value of 0.5 corresponds to VOCs like trichloroethylene.

Chemical Concentrations, C_{win}

Although many VOCs are not detected in municipal wastewater, concentration values were estimated to range from between 10 and 3,000 mg/m^3. An upper-band of 3,000 mg/m^3 is very high for most municipal sewers, but is reasonable for highly-industrial municipal sewers as well as most on-site industrial sewers.

Flowrates, Q_w

Flowrates in sewers can approach zero, but can exceed hundreds of millions of gallons per day in the interceptors of some large urban areas. For this study, a range of 0.003 m^3/s to 0.61 m^3/s was used, i.e., consistent with water use for populations ranging from 1,000 to 200,000, with a daily wastewater flow per capita of 0.265 m^3/c-d [*12*]. A "typical" flowrate of 0.15 m^3/s was selected.

Air Entrainment Rates, Q_e

The values for Q_e were based on McLachlan et al. [11]. For non-disintegrating jets, air entrainment rates may be as high as six times the liquid flowrate, while for disintegrating jets, air entrainment rates may be as high as thirty times the liquid flowrate.

Air Flowrate, Q_a

Both the typical and maximum gas flowrates were taken to be 1×10^{20} m^3/s which effectively corresponds to infinite ventilation (i.e., the gas concentration equals zero at all times). For lack of any published values, the minimum air flowrate was arbitrarily estimated to be 2.5×10^{-3} m^3/s.

Splashing & Disintegrating Droplets, $Q_{sd}\gamma_{sd}$, $Q_{dd}\gamma_{dd}$

The splashing and disintegrating droplet mechanism has both uncertain flows and degree of equilibrium. The maximum value of the combination $Q_{sd}\gamma_{sd}$ is the total hydraulic flow Q_w. For this maximum to be reached all of the water would have to become splash droplets, i.e., $Q_{sd} = Q_w$, and those droplets would have to fully equilibrate while in the headspace ($\gamma_{sd} = 1$). The value of the combination $Q_{sd}\gamma_{sd}$ is set as a fraction of the hydraulic flow, Q_w. The typical fraction is arbitrarily set at 0.005. The minimum and maximum values are set at 10^{-5} and 0.3 respectively, to cover the conceivable domain.

Disintegration droplets are treated identically.

Degrees of Equilibrium (γ_{ff}, γ_e, γ_{surf})

The degrees of equilibrium vary from 0 to 1.

For the falling film, based on the short time the water film is falling, it is unlikely that equilibrium is approached. Therefore, a typical value of γ_{ff} is suggested as 5%, and would not likely be outside the range of 0.001% to 50%.

The degree of saturation of the entrained air bubbles, γ_e, was assumed to be 1.0 for very large waterfalls [11]. For this study, a typical γ_e value of 0.5 was assumed, with a range of 0.1 to 1.0.

The degree of equilibrium for the tail water surface (γ_{surf}) was set to 10^{-5}, 0.005 and 0.3 for minimum, typical and maximum, respectively.

STRIPPING ESTIMATE RESULTS AND DISCUSSION

A summary of predicted emissions resulting from the substitution of the values given in Table 2 into the emissions equation (Eq. 12) is provided in Table 3. The emissions are reported as a percentage of the VOC that volatilizes according to Eq. 13. The linear relationship between the emissions and the inlet concentration allows the concentration parameter to be removed from the analysis.

TABLE 3. Relative Contribution by Mechanisms to Emissions

Mass Transfer Site	Typical	Minimum	Maximum
% Volatilized	73%	1%	98%
Falling film	7%	1%	51%
Disintegrating Drops	1%	1%	8%
Splashing Droplets	0%	1%	0%
Tailwater Surface	0%	1%	0%
Air Entrainment	92%	96%	41%

For "typical" conditions, 73% of the contaminant in the wastewater is estimated to volatilize into the atmosphere as the wastewater passes over a "typical" drop structure. For the maximum conditions, it is estimated that 98% of the contaminant is emitted to the atmosphere. For the minimum conditions, it is estimated that only 1% of the contaminant is stripped to the atmosphere.

Thus, for the range of drop structures that may realistically prevail, it is possible that the amount of VOC of stripping can range from almost 100% to almost 0%. This feature has both positive and negative implications. It means that to reliably estimate emissions for a single drop structure, some specific information is required as outlined in model development. The wide range in stripping also suggests that drop structures could be designed to minimize emissions. However, while this model cannot directly describe how to change the design, it may give some guidance by identifying controlling mechanisms.

Table 3 also includes the relative contribution by each mechanism to overall stripping. It is apparent that air entrainment is the controlling mechanism for the typical scenario. Stripping from the tailwater surface and splashing droplets were minimal in all three cases. These results are significant in so much as they suggest that the focus of future research should be placed on one or two key mechanisms.

The two key mechanisms appear to be air entrainment and evaporation from a falling film. For air entrainment mechanism, the research needs include effective techniques at predicting and controlling entrainment rates and factors that influence bubble size and retention in the tailwater, which influence the degree of equilibrium achieved. For the falling film, the factors that influence the mass transfer behavior and coefficient of the film and thus the degree of equilibrium achieve requires further exploration. It would seem that this is more important for structures that have a higher overall stripping efficiency.

Although the model presented incorporates five mechanisms it still has considerable simplicity. Many of the parameters have an interdependency that has not been fully incorporated into the model. Some of the interdependency has been incorporated such as the link between the air entrainment and the total water flow. The dependency utilized is a linear relationship that has been suggested by MacLachlan et al. [11]. Other dependencies between parameters have not been incorporated, such as the link between the degree of equilibrium achieved and the Henry's Law constant and on the hydraulic flow. Ultimately, it is important to incorporate all of these interdependencies.

A second manner in which to consider the model is to investigate the impact each individual parameter has on stripping. This was done by completing a sensitivity analysis in which each parameter was varied over its range of reasonable values (minimum to maximum), while retaining the other parameters at their "typical" value. Table 4 summarizes the range of stripping efficiencies obtained and is sorted by parameters leading to the largest range in percent volatilized. The results indicate that for five of the parameters the possible variation in stripping efficiency is significant and that for the other five parameters the possible variation is more subtle.

TABLE 4. Ranges of Stripping Efficiencies Over Operating Range of Parameter Values

Parameter	% Volatilized	Difference
C_g/Q_a	73–1	72[a]
Q_e	25–89	64
Q_w	99–42	55
H_c	41–93	52
γ_e	37–84	47
γ_{ff}	72–86	14
$Q_{dd}\gamma_{dd}$	73–81	8
γ_{surf}	73–75	2
$Q_{sd}\gamma_{sd}$	73–75	2
C_{win}	73	0

[a] Only two cases were modelled: high air flowrate – minimum C_g (vol. = 73%); low air flowrate – high C_g (vol. = 1%)

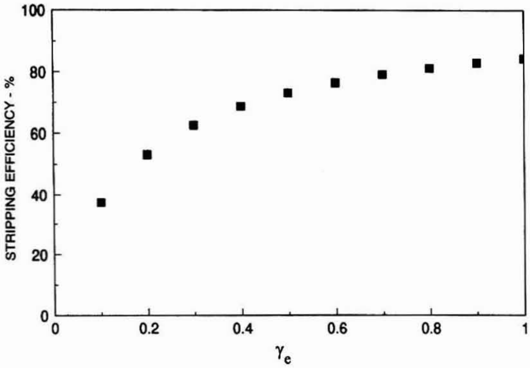

FIGURE 2 Stripping efficiency versus γ_e.

The most significant parameter is the ventilation rate, which has a role in all of the mechanisms. The ventilation rate for partially enclosed structures is difficult to quantify, and ths analysis indicates that if reliable emission estimates are to be obtained, then reliable ventilation rates are required.

The second and fifth parameter (Q_e and γ_e) are both associated with the air entrainment mechanism and reinforce the necessity of accurately quantifying these parameters.

The third and fourth parameters are the hydraulic flow and the Henry's law coefficient, respectively. Although these are important and can vary over a wide range, both are readily established with reasonable reliability for a specific situation.

Figures 2, 3, and 4 show the stripping efficiency's dependence on the degree of equilibrium of entrained air bubbles, the air entrainment rate and the Henry's Law coefficient, respectively. It is apparent that for each of these parameters there is not a linear relationship between the stripping efficiency and the parameter. In general, over the expected ranges of γ_e, Q_e and H_c, the most significant increase in volatilization occurs with a small change in the parameter value at the lower end of the range. Thus, accurate values are particularly important for these parameters when they fall in the lower range of possible values.

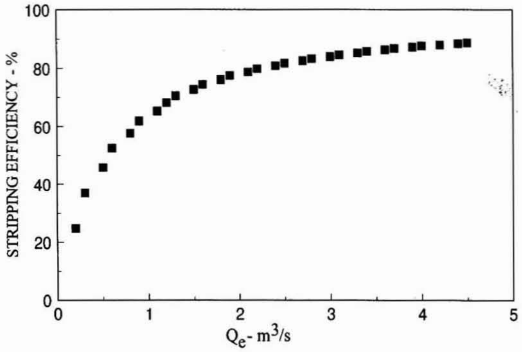

FIGURE 3 Stripping efficiency versus Q_e.

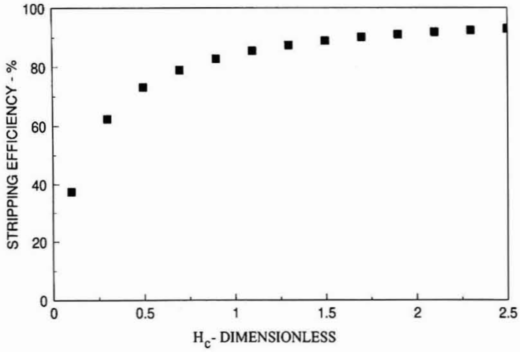

FIGURE 4 Stripping efficiency versus H_c.

SUMMARY

A mechanistic model has been developed to estimate VOC stripping from drop structures in WWTPs. It accounts for five mechanisms associated with mass transfer at the drop. It appears that the mechanism associated with air entrainment is the most significant process under a wide range of conditions. Further study of the physical air entrainment process is warranted. Stripping from the falling film is the second most significant mechanism.

A sensitivity study for the parameters studied over the operating range of the conditions identified was completed. It indicated that the largest variation in stripping is associated with air entrainment, liquid and air flow, Henry's Law coefficient and degree of saturation for entrained bubbles. These parameters are required to be known with the greatest amount of certainty.

ACKNOWLEDGEMENTS

The authors acknowledge constructive discussions with Dr. H. Melcer of Brown and Caldwell, Seattle, WA, Dr. J. Bell and Mr. H. Monteith of Enviromega, Hamilton, Ontario, and Dr. W. Parker, Carleton University, Ottawa, Ontario. Funding for this research has been provided by a Water Environment Research Foundation Contract through the Wastewater Technology Centre in Burlington, Ontario.

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Process Challenges in Rotary Kiln-Based Incinerators In Soil Remediation Projects

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Most Superfund sites undergoing thermal remediation consist of high-moisture content (15 to 40 percent) soils having light organic contamination (low-heat content). In the early 1980s, the rotary kiln incinerators employed at these Superfund sites were relatively small mobile hazardous waste incinerators (HWI) built on standard-size semi-trailers. As the industry matured over the past ten years, competition has driven the industry to larger and more efficient rotary kiln systems that minimize the cost per ton of soil treated by increasing the throughput rates and shortening on-site processing time.

Because these units are transported from site to site by truck or a combination of rail and truck, the rotary kiln outside shell diameters have peaked to approximately 13.5 feet. Now the focus has shifted to increasing the processing capacity of these existing, maximized fixed-sized systems. Such actions include the use of oxygen-based combustion systems, which increase the throughput and efficiency by improving heat transfer and reducing the volume of combustion gas requiring treatment. However, despite the experience and expertise gained by the participants in the thermal remediation industry, many of the same process challenges still remain. Combustion gas particulate entrainment from a rotary kiln HWI is a key issue when thermally treating soils because of the slagging potential in the secondary combustion chamber (SCC) and/or the potential to overload the downstream incinerator wastewater treatment system (IWTS). Excessive infiltration air into the rotary kiln can reduce the rate of heat transfer to the solids bed and correspondingly reduce the overall processing rate. More stringent ash quality requirements require higher ash temperatures and longer solids retention time at temperature. Estimating metal emissions remains a challenge due to the limited availability of data on metal behavior in combustion systems. New and more stringent particulate, nitrogen oxides (NO_x), metals, and dioxins/furans emissions performance requirements present additional challenges, as does a trend in towards zero-liquid discharge from the air pollution control system.

This article discusses these process challenges facing the industry and potential solutions, based on data from IT's Hybrid Thermal Treatment System® HTTS® and other sources.

INTRODUCTION

Typical Transportable Incinerator

A typical transportable, HWI deployed at a Superfund site consists of an incineration module, an APCS, and other site-specific ancillary systems. The incineration module consists of a rotary kiln incinerator, and a secondary chamber that oxidizes off-gases from the rotary kiln. The APCSs may be wet, dry, or dry-wet systems depending on the waste or soil profile encountered in a given site, the emission criteria to be met, and the contractor's technology preference. A wet scrubber-based APCS typically includes an integral incinerator wastewater treatment system (IWTS) that removes the suspended solids and chemically treats the water, in some cases, prior to discharging the water to a publicly operated treatment works (POTW) or on-site wastewater treatment system (WTS). The solids discharge from the dry (baghouse-based) and dry-wet APCS is landfilled on or off site depending upon the clean-up criteria and/or regulatory requirements.

IT's modular and transportable HTTS® consists of a 13.5-foot-outside diameter by 75-foot-long countercurrent rotary kiln, a down-fired SCC, and a wet APCS (Acharya *et al.* [*1*]). A block flow diagram of the HTTS® process is shown in Figure 1. IT has cloned the basic HTTS® design and deployed it in various configurations at multiple Superfund sites including the following:

- The Cornhusker Army Ammunition Plant (CAAP) near Grand Island, Nebraska, incinerating 22,000 tons of explosives contaminated soil.
- The Louisiana Army Ammunition Plant (LAAP) site in Bossier City, Louisiana, incinerating 108,000 tons of explosives contaminated soil.
- MOTCO Hazardous Waste site, a National Priorities List (NPL) site in LaMarque, Texas, incinerating 12,100,000 gallons of liquids; 3,200,000 gallons of sludge, tars, and solids; and 21,300 cubic yards of soils and debris.
- The contaminated waste material at the Sikes Disposal Pits (Sikes) site in Harris County, Texas, incinerating nonpumpable sludges, tarry sludges, sandy soil, clay soil, more than 2,000 drums, trash, trees, metal debris, etc. in excess of 500,000 tons. The Sikes remediation was an IT-Davy joint venture.

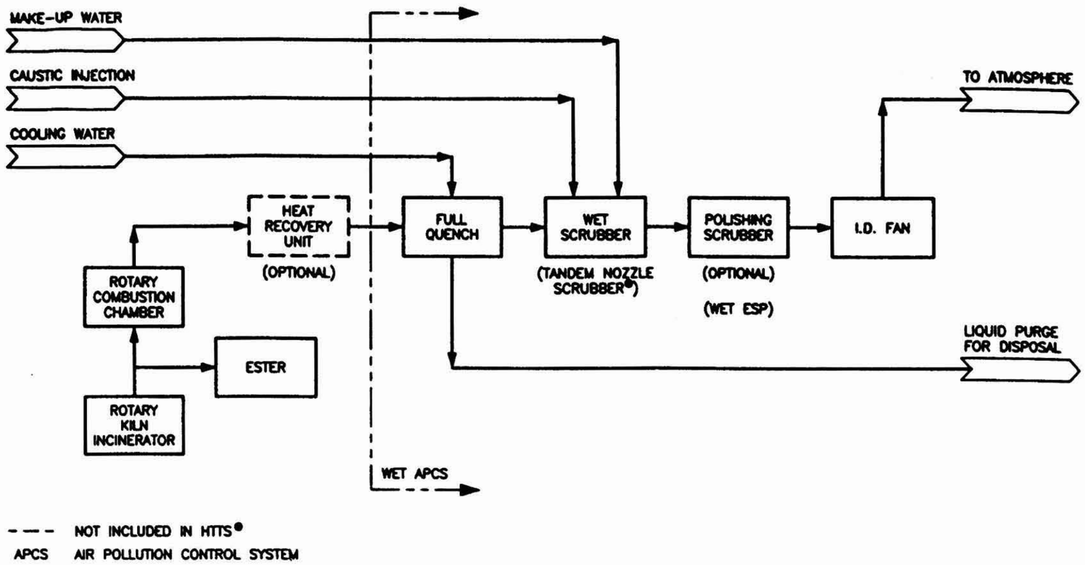

FIGURE 1 Block flow diagram of IT's HTTS® with wet air pollution control system.

- The Bayou Bonfouca (BB) Superfund Site in Saint Tammany Parish, Louisiana, incinerating 150,000 tons of creosote contaminated bayou sediments and soils. The BB remediation is a joint venture with OH Materials Corporation (OHM).
- The BB contract was amended in July 1995 to include approximately 50,000 tons of additional polyaromatic hydrocarbon (PAH)-contaminated soils and materials from the Southern Shipbuilders Corporation (SSC) Superfund Site also in Saint Tammany Parish. The SCC materials are to be transported to the HTTS® at the BB site for thermal treatment and then transported back to the SSC site for final internment.
- The Times Beach, Missouri on-site incineration of approximately 103,000 tons of dioxin-contaminated material.

Process Challenges and Potential Solutions

The process challenges can be categorized as combustion-related challenges and APCS-related challenges. Since most Superfund sites involving thermal remediation to date have primarily been soils (15 to 40 percent moisture) with light organic contamination (low-heat content, typically less than 2,000 Btu/lb), this article focuses on the process challenges in the combustion and APCS modules treating this type of soils.

COMBUSTION RELATED CHALLENGES

The following sections discuss some of the major combustion-related challenges in treating Superfund soils and approaches to resolving or minimizing these problems:

System Capacity

The system capacity is the key factor in today's soil remediation industry. The higher the soil processing rate (tons per hour [tph]), the lower the dollar per ton of soil ($/ton) processed. With most on-site thermal remediation projects, increasing processing capacity and on-stream time will help minimize time on site, thus improving overall project economics. The price per ton also reflects fixed mobilization, systemization, and demobilization costs. Consequently, as the soils tonnage increases, the price per ton of soil thermally treated decreases.

In the early 1980's, the industry built mobile HWIs on standard-size semi-trailers that processed up to 5 tph of low-heat content, typically less than 2,000 Btu/lb, soil with 15 to 40 percent moisture. In the mid 1980s, the industry started building transportable HWIs that processed 10 to 15 tph of soil. Over the last 10 years, the industry trend has been to build increasingly larger transportable incinerators to increase processing capacity. However, to be transportable on semi-trailers, the maximum kiln outside diameter is limited to approximately 13.5 feet.

The cost of thermal treating lightly contaminated soils at Superfund sites ranges from $200 to $300 per ton. For large Superfund remediations, greater than 100,000 tons, the economics of scale tend to favor the larger throughput systems, greater than 20 tph. The large units are able to spread their higher mobilization cost over a large tonnage and short time frame resulting in an overall lower cost per ton of soil treated than small throughput systems. For small Superfund remediations, 50,000 tons or less, the economics tend to favor smaller throughput units, 10 tph or less, particularly for sites having less than 30,000 tons. The higher fixed mobilization costs for the large systems simply make them much less competitive with the smaller throughput units for remediations jobs of this size. Between 50,000 and 100,000 tons, the daily fixed costs of operation and the total time on-site combine with mobilization costs to make the economics very competitive for both large and small systems.

Oxygen-Based Combustion Impacts and Benefits

A proven method of increasing incineration system processing capacity without increasing equipment size is to utilize an oxygen-based combustion system. When pure oxygen is used in place of air for oxidizing auxiliary fuel and/or organics from the soils being treated, the amount of nitrogen in the combustion zone, which acts as a diluent and heat sink, is reduced.

An APCS is volumetrically limited in its ability to treat combustion gases. The reduction in combustion gas volume per ton of soil treated by using oxygen in place of air for combustion means that incinerator throughput can be increased with no modifications to the downstream APCS.

The other major factor in limiting the treatment rate of lightly contaminated soils is their moisture content. To achieve destruction of the organics in the soils, the water in the soils must be first evaporated. Once dried, sensible heating of the soils vaporizes the organics in the soils. Excess oxygen and heat in the combustion zone oxidizes the vaporized organics. Using oxygen in place of air for auxiliary fuel combustion means that heat normally absorbed by the nitrogen is available to evaporate moisture and for sensible heating of the soil.

Several oxygen-based combustion system options are presently available. These options include combustion air enrichment, oxygen lancing, and oxygen-burners. With combustion air enrichment, oxygen is injected into the burner air supply (primary or secondary). Oxygen lancing involves injecting pure oxygen through a lance pipe into the combustion chamber to augment combustion air. Oxygen-burners use pure oxygen instead of air to oxidize auxiliary fuel. A combination of these methods can be used, such as an oxygen-burner in the rotary kiln and combustion air oxygen enrichment or oxygen lancing in the SCC. Oxygen lancing or combustion air enrichment to reduce the volume of secondary combustion air should be seriously considered when there is a relatively high heat content in the solids, greater than 4,000 Btu/lb. Oxygen burners are more suited when high burner firing rates are required as in processing high-moisture, low heat content wastes or soils, less than 2,000 Btu/lb as described above, where heat transfer is more critical (Acharya *et al.* [2]).

IT evaluated two oxygen-based combustion system options for the BB Superfund project. The contaminated material feed rate was estimated at 15 to 20 tph for the oxygen lance option and 20 to 25 tph for the oxygen-burner option. These rates were based on an air infiltration rate into the combustion system of 3,000 to 5,000 standard cubic feet per minute. It is critical that air infiltration be minimized to realize the full benefits of using an oxygen system. The net savings, after the cost of oxygen, were estimated at \$1.0 to 2.2 million for the oxygen lancing and \$2.2 to 2.7 million for the oxygen-burner option. These estimates were based on an estimated project operating savings of \$500,000 per month due to the reduction in the total burn time for both the options. These significant savings led IT to retrofit the HTTS® rotary kiln with an oxygen-burner for the BB project (Acharya *et al.* [2]). Although equipped to do so, injecting oxygen into the SCC was not used at BB. During the BB trial burn, IT's HTTS® unit was unable to treat soils at an average rate of just over 29 tph. The project is proceeding ahead on schedule and under budget.

Higher nitrogen oxide (NO_x) emissions (on a volume concentration basis) are a potential drawback when employing an oxygen-burner system. NO_x emissions with air-based burner systems are typically in the 60 to 80 parts per million dry volume (ppm_{dv}) range, while emissions with an oxygen-based combustion system can be 120 to 480 ppm_{dv} (Acharya *et al.*, 1995). However, the pounds of NO_x emitted per ton of soil treated is lower for oxygen-based burner systems compared to air-based burner systems. The impacts of NO_x from lancing of oxygen into the combustion chamber or combustion air enrichment were not reviewed for this article. There are no Resource Conservation and Recovery Act/ Toxic Substance Control Act (RCRA/TSCA) criteria for NO_x, but, local, state, and federal ambient air quality standards must be met. The allowable NO_x emissions are determined on a project-specific basis.

Because the oxygen and auxiliary fuel are burned at close to stoichiometric ratios in the oxygen burner, the flame temperature exceeds 3,500°F. At this temperature, conversion of nitrogen to NO_x is very favorable. In a rotary kiln, there will always be some nitrogen from infiltration air. Air infiltration in a rotary kiln is not only unavoidable but necessary in some degree to maintain the cooling of the rotary seals. However, the key to minimizing NO_x formation when using an oxygen burner in the rotary kiln is to minimize the amount of infiltration air especially on the burner end. NO_x emissions during the BB trial burn averaged under 100 ppm because air infiltration was minimized.

Due to higher flame zone temperature for oxygen-based burners compared to air-based burners, slagging potential exists in the kiln. IT's experience indicates that the slagging potential can greatly be reduced by locating the burner well above the solid bed and allowing some infiltration air to cool the flame zone.

Excess Air Infiltration

Excess infiltration air can significantly reduce the soil processing capacity in a rotary kiln, because part of the burner thermal output must be used to heat the infiltration air, thereby reducing the heat transfer to the solids bed. In a countercurrent rotary kiln, this impact is greater if the air infiltrates into the ash discharge end of the kiln. In the countercurrent case, the infiltration air must pass through the entire length of the kiln and must be heated to the kiln operating temperature. As the infiltration air to the system increases the gas flow through the rotary kiln increases, decreasing overall system capacity. Infiltration air in the discharge end of a co-current rotary kiln system has a negligible effect on the rotary kiln operation, but because the infiltration air at this point moves directly to the SCC, more auxiliary fuel usage is required in the SCC to maintain temperature. In both the countercurrent and cocurrent rotary kiln cases, the impact of the air infiltration in the combustion zone reduces soil throughput capacity by absorbing heat that would otherwise go toward treatment of more soil or combustion gases resulting from the treatment of soils.

In both the countercurrent and cocurrent rotary kiln cases, the impact of the air in-leakage into the APCS, where the draft is the highest, is even more severe from a gas volume viewpoint than it is in the combustion zone. The induced draft fan size is fixed, therefore, air infiltration in the APCS offsets the amount of combustion air that can be drawn though the combustion zones and also correspondingly reduces throughput capacity.

As air infiltration to the rotary kiln using an oxygen-burner increases, thermal NO_x generation can increase due to the availability of additional nitrogen. Typically, NO_x

formation is less in countercurrent kilns compared to cocurrent kilns, because of the location of the feeding device and the burner. In cocurrent rotary kilns, the burner and the feeding device are located at the same end of the kiln, and infiltration air through the feeding device tends to pass through the burner zone, forming additional NO_x.

The infiltration of air into the system can be detected by visual inspection and by obtaining oxygen and carbon dioxide profile data at various locations in the system. The infiltration air rate to the system can be quantified by performing oxygen and nitrogen material balance calculations across the system. Another method to quantify the air infiltration rate is to use a pitot-tube at suspected infiltration locations. The suspected locations should be regularly maintained to minimize the air infiltration.

Well designed kiln seals at either end of the kiln are essential to limiting air infiltration. Rotary kiln seal design, as with APCS selection, is very much dependent on contractor's technology preference or experience with a particular seal.

Other areas of significant air infiltration are the feed and ash handling systems. The use of screws or double tipping valves/slinger belts are the two good choices of soil feed systems that minimize air infiltration. While screw systems may provide a generally tighter seal to air infiltration, double tipping valve/slinger belt arrangements tend to be more operationally flexible. Optimum operation of either type of feed system requires that the feed material be screened to remove roots, rocks and other oversize debris that can mechanically jam the feed system. Rocks or similar hard debris in the screened soils can still present a problem for most all screw feeders while double tipping valves are generally unaffected by these items. On the other hand, tree roots or other long, thin debris that can pass through the screening operation may jam a double tipping valve while the screw feeder would have little or no problem with such debris.

Another factor in feed handling is the moisture content and its impact on feed handling characteristics. The feed material must be dried to the optimum handling moisture. The optimum moisture content is matrix specific. Generally with low clay content soils, screw feeders and double tipping valves/slinger belts work equally well. The moisture content of these types of soils are less critical than for high clay content soils. The stickiness of high clay content soils is very dependent upon moisture content. Sticky, rock free clay soils can still jam a screw feeder or double tipping valve arrangement, but generally, the double tipping valves experience less difficulty on this type of soil. Operational experience with the specific soil matrix is usually the only way to determine the optimum drying for best material handling of clay type soils. For stubbornly sticky clay type soils, blending with lime or sand can sometimes improve their handling qualities.

On the ash handling end of the kiln, screws or double tipping valves generally work equally well except if rocks are present. Rocks can jam a screw feeder. A high degree of abrasion will also occur if screws are used to handle the dry soils. As with the feed end, care must be taken in moisturizing the ash from clay type soils so as not to reach the sticky stage that can present problems. Again, operational experience with the specific soil matrix is usually the only way to determine the optimum degree of ash moisturizing for best ash material handling quality.

Ash Quality

Ash quality is a key criterion in any soil remediation site. Ash quality, normally dictated by a site specific Record of Decision (ROD), may include maximum limits for organics and regulated metals. The concentration limits of organics in ash are met by proper selection of rotary kiln operating temperature and solids retention time. The "time at temperature" relationship is normally based on laboratory/pilot-scale tests and is then fine-tuned in the field. Ash not meeting the metals criteria must be stabilized by addition of lime or Portland cement. Again, bench scale testing of laboratory prepared ash is necessary to determine the proper ratio of soil and stabilizer to physically and chemically immobilize the metals.

The process challenge is that the "solid residence time at temperature" relationship is project-specific and can vary depending on the type and concentration of organics in the feed, ash criteria to be met, the soil matrix impacts, type of the incinerator (cocurrent versus countercurrent rotary kiln), and the incinerator operating conditions. Therefore, it is suggested that these parameters be examined at least at the bench-scale level to determine processing capacity and to avoid expensive ash re-burn during commercial operation.

IT typically performs bench-scale laboratory tests on the actual soils using a rotary tube apparatus (RTA). The RTA is a 4-inch diameter by 20-inch long externally heated allow tube which IT uses to simulate rotary kiln conditions and to determine the optimum "time at temperature" relationship required to meet the ash criteria. Additional pilot-scale testing may also be performed to establish the operating conditions for the commercial system. The application of the bench- and pilot-scale data are important in meeting the ash quality at design capacity for a given project.

The ash criteria and ash decontamination performance at the BB remediation project and Sikes Superfund remediation project are presented in Table 1. Multiple criteria were dictated by the ROD for Sikes while BB must only meet a single criterion for total polynuclear aromatics. The time at temperature relationship was established solely on bench-scale testing for the Sikes project while bench- and pilot-scale tests were conducted for the BB project. In both cases, the site-specific criteria were easily met.

Metals Emissions

The metals of regulatory concern are arsenic, cadmium, chromium, beryllium, nickel, antimony, barium, lead, mercury, selenium, silver, and thallium (Dempsey *et al.* [3]). These metals exit the thermal treatment system in the bottom ash, the APCS residues, and the stack emissions. The metals in the ash and APCS residues are normally handled in accordance with the ROD criteria. The metals that are discharged to the atmosphere in the stack emissions are the primary concern.

Metal volatility is the key parameter that determines the partitioning of a metal/metal compounds to the incinerator bottom ash or to the APCS (Dempsey *et al.* [3]). In general, the lower the volatility, the lower the metal partitioning to the APCS. Metals volatility can be affected by a combination of factors including soils temperature and chlorine content. Metal partitioning is greatly influenced by the soil matrix conditions and operating conditions, primarily ro-

TABLE 1. Ash Criteria and Ash Decontamination Performance at Sikes and Bayou Bonfouca Project

	Sikes Project		Bayou Bonfouca Project	
Parameter	Maximum Allowable Concentration (ppm)	Actual Concentration (ppm)	Allowable Concentration (ppm)	Actual Concentration (ppm)
Volatiles				
Benzene	10	< 1	NA	NA
Chlorobenzene	10	< 1	NA	NA
Chloroform	10	< 1	NA	NA
1,1-Dichloroethane	10	< 1	NA	NA
1,2-Dichloroethane	10	< 1	NA	NA
Ethyl benzene	10	< 1	NA	NA
Methylene chloride	10	< 1	NA	NA
Tetrachloroethylene	10	< 1	NA	NA
Toluene	10	< 1	NA	NA
Trans-1,2-dichloroethylene	10	< 1	NA	NA
Trichloroethylene	10	< 1	NA	NA
Total polynuclear aromatic hydrocarbons	100	< 50	10	< 8
Metals EP Toxicity				
Arsenic	5.0	0.5	NA	NA
Barium	100.0	10.0	NA	NA
Cadmium	1.0	0.1	NA	NA
Chromium	5.0	0.5	NA	NA
Lead	5.0	0.5	NA	NA
Mercury	0.2	< 0.02	NA	NA
Selenium	1.0	< 0.1	NA	NA
Silver	5.0	< 0.5	NA	NA

Note: NA-Not Applicable

tary kiln temperature. For example, most clay type soils tend to have low metals volatilities. The challenge is in the selection of more accurate partitioning factors and removal efficiencies for a given system.

As part of its strategy to control metal emissions, the U.S. Environmental Protection Agency (EPA) developed estimates for partitioning of metals in the incinerator and for removal of metals in different APCSs available in the market. However, the EPA factors are so overly conservative that they are practical only for cursory screening of potential metals emissions. More accurate data can be obtained from trial burn data, literature searches including computer data bases such as Compendix Plus (an environmental index), previous studies performed by EPA's Combustion Research Facility in Jefferson, Arkansas, and conference papers.

The metals emissions estimates are made using anticipated system metal removal efficiencies that include metals partitioning to the incinerator bottom ash and removal in the APCS. The estimated emissions are then compared to the allowable emissions per Tier I, II, or III allowable emissions as defined in EPA guidance and Boiler and Industrial Furnace (BIF, 40 CFR 266 Subpart H) regulations. In addition to anthropological sources of metals contamination, ubiquitous or native levels of regulated metals in soil will often be significant enough to impact incinerator operations. Because EPA allows no credits or corrections for such native metals levels in soils, the thermal treatment system operator is usually forced to consider more expensive site-specific Tier III analysis in order to determine metal feed rates and emission rates that may be achievable with current technology, even when the anthropological metal contamination alone would not dictate such actions.

Generally, the system removal efficiencies for the wet APCS on IT's HTTS®, which include partitioning to the bottom ash and removal by the APCS, are typically greater than 97% for all metals in soils except for lead and mercury. For lead, system removal efficiencies can be as low as 65%. For mercury, system removal efficiencies can range from as low as 25% to as high as 90% or greater.

Particulate Entrainment

Particulate entrainment from a rotary kiln incinerator is an operational issue because of its impact on the downstream SCC and APCS equipment and the potential to reduce the on-stream factor of the entire system. Accurate estimation of the amount of particulate carry-over from a rotary kiln and the particle size distribution (PSD) of that carry-over material is crucial to estimating the quantity of particulate settling at the bottom of the SCC and particulate loading in the IWTS (needed for equipment selection and sizing purposes). Additionally, particulate slagging potential exists in the SCC. The amount of particulate carry-over from a rotary kiln may depend on the kiln type (cocurrent versus countercurrent), and type of soil (sand, silt, clay, and the mixture of the three), the mode of operation (oxidative versus pyrolytic), the combustion gas velocity through the kiln, the presence or lack of flights inside the kiln, the percent solids loading, the fines fraction in the solids, the interior wall roughness, the exit dam geometry, the solids feed rate, and the feed system.

Under the unified soil classification system (USCS) (American Society for Testing and Materials [ASTM] Standards, 1991 [*4*]), soils may be classified as sand, silt, and clay if their respective particle sizes are greater than 7.5 microns (sieve No. 200), 0.5 to 7.5 microns, and less than 0.5 microns. IT's experience when treating sandy soils indicates that 7 to 10 percent of the wet soil feed to a smooth, refractory lined kiln operating at 1.5 to 2 revolutions per minute (rpm) will carry over to the APCS. Very little literature data exists for silt or silt/clay type soils. For silt and silt/clay type soils, one would expect the entrainment rate to be generally higher because of the smaller PSD of clays. However, based on pilot-scale testing performed by IT of a countercurrent rotary kiln processing dewatered bayou sediments (silt/clay-type soils), IT found the entrainment rate was as low as 2 percent of the wet feed rate with the largest size particulate to be carried to the SCC being 70 microns (Acharya, P., Prabhu, S., *et al.* [*5*]). Under certain conditions, the clay may act as a binder and impede the particulate entrainment. Based on these test results, blending silty soils with clay may lower particulate carry-over in commercial operations. For accurate entrainment estimates for a given soil matrix, project specific pilot-scale testing is advised.

Ash/Particulate Slagging Potential

Slagging of ash in the kiln and particulate in the SCC can adversely impact the incineration operation, and thereby reduce the overall operating factor for the entire system. The solid bed/ash in the kiln may slag depending on the factors such as the type and location of the burner in the kiln, the mineralogical composition of the solids, and the solids retention time at ash discharge temperature. The particulate leaving in the rotary kiln off-gases may slag in the SCC. The potential for slagging in the SCC is dependent on the SCC burner design, the mineralogical composition of the particulate, whether the kiln off-gases are fully or partially oxidized, and SCC operating temperature. Therefore, it is critical to perform bench-scale slagging potential tests prior to the incinerator design.

Typical bench-scale slagging potential tests include measurement of ash PSD, chemical identification of the ash including elemental and mineralogical composition, and determination of the melting point of the ash including time versus temperature relationships. A typical mineralogical analysis of soil needs to include analysis for silica (SiO_2), fluxing agents such as CaO and Na_2O, and alkali metals, such as Na, K, and Ca. Generally, the higher the SiO_2 content, the higher the soils melting point, which is preferred. The more fluxing agents present, the better the slag will flow if slagging were to occur. CaO content can be high, especially when lime is added to the feed soil for materials handling purposes. Alkali metals can drastically reduce the melting point of the ash. A hot stage microscope can be used to determine the temperature at which most of the ash sample melts. This temperature should be higher than the planned SCC operating temperature to avoid slagging.

Based on these relatively inexpensive tests, the potential causes for slagging are determined and appropriate system design changes can be made. If the slagging is inevitable due to the composition of the soil, the nature of the kiln off-gases (fully or partially oxidized) or SCC operating temperature, fluxing agents such as lime can be blown into the SCC to enable the slag to flow more easily so that it can be collected and removed on a continuous basis. Burners installed at strategic locations can also keep isolated portions of the system hot to help avoid slag build-up.

Combustion-Related Emissions

The combustion-related emissions are Principal Organic Hazardous Constituents (POHC), Products of Incomplete Combustion (PIC), carbon monoxide (CO), total hydrocarbons (THC), and dioxins/furans. In EPA's opinion, the first stage in a combustion process is the immediate thermal decomposition of the POHCs in the flame zone to form less complex compounds, also referred to as PICs (Acharya, P., DeCicco, S. [*6*]). Most of these PICs are rapidly decomposed to form CO. The second combustion stage involves the oxidation of CO to CO_2. This is the slowest (or rate limiting) step in the process as CO is more thermally stable than the PICs. When CO is low, THCs are low. In most HWIs, POHCs, CO, and PICs measured as THCs and dioxins/furans are far below the RCRA or ROD driven criteria as shown by the data presented in Table 2.

The available data indicate that if the combustion temperature is maintained higher than 1600°F, at a typical residence time of 2.0 seconds, essentially all but trace amounts of organics in the combustion gas are destroyed provided there is adequate air/fuel mixing and excess oxygen (greater than 3%) (Acharya, P., DeCicco, S. [*6*]). This is true even for compounds such as dioxins/furans and PCBs. A conventional "3-Ts" (time, temperature, and turbulence) approach to good combustion practice will result in efficient destruction of trace organics and CO. Time and temperature are obvious factors, but turbulence can be very important. Burner configurations in the SCC that impart a spin to the combustion gas and/or throttling of the gases within the SCC will improve the turbulence and thus organic destruction efficiency in the SCC.

AIR POLLUTION CONTROL-RELATED CHALLENGES

The APCS technology is constantly undergoing improvements to meet the changing particulate, acid gas, metals, and dioxins/furans emissions, and plume suppression requirements. Additional equipment installation and process condition changes are often required to meet more stringent regulations. The regulator trend is towards zero-liquid discharge from HWIs, forcing the industry to install dry or dry-wet APCSs that discharge solid by-products. When compared to wet scrubbers, dry or dry-wet APCSs have better removal efficiencies for some pollutants. The frequency of APCS types deployed at Superfund sites, in descending order, are the wet, dry, and dry-wet systems.

Typical Process Flow Diagram for Wet APCS

A wet APCS consists of a full adiabatic quench in which water is sprayed to the incoming gases. The gases are cooled to an adiabatic saturation temperature of 180 to 200°F before the gases enter a wet scrubber. IT's wet

TABLE 2. Comparison of Trial Burn Data for the Wet APCS, Dry APCS and Dry-Wet APCS · at Sikes, Bayou Bonfouca, Sauget, and Old Midland Projects

		Wet APCS				Dry APCS		Dry-Wet APCS	
		Bayou Bonfouca Project		Sikes Project		Sauget Project		Old Midland Project	
Parameter	Units	Objective	Actual Emissions[a]	Objective	Actual Emissions[b]	Objective	Actual Emissions	Objective	Actual Emissions[c]
Solid feed rate	mtph (tph)	22.5 (25)	25.5 (28.5)	—	40 (44.1)	—	4.5 (4.1)	—	16 (18.1)
DRE = Carbon tetrachloride	%	≥ 99.99	—	—	—	≥ 99.99	99.9995	—	—
DRE = Toluene	%	≥ 99.99	≥ 99.998	—	—	—	—	≥ 99.99	≥ 99.9998
DRE = Naphthalene	⊨	≥ 99.99	< 99.997	≥ 99.99	99.9955	—	—	—	—
DRE = Anthracene	%	≥ 99.99	< 99.997	—	—	—	—	—	—
DRE = Chlorobenzene	%	—	—	≥ 99.99	99.99999	≥ 99.99	NA	≥ 99.9999	≥ 99.999932
DRE = Trichlorobene	%	—	—	—	—	≥ 99.99	99.99999		
DRE = Hexachloroethane	%	—	—	—	—	< 99.99	99.99996		
HCl removal efficiency	% or kg/hr (lb/hr)	> 99% or < 1.8 (4), whichever is higher	< 0.02 (0.036)	< 1.8 (4)	0.01 (0.027)	> 99% or < 1.8 (4), whichever is higher	1.3 (2.8)	> 99% or < 1.8 (4), whichever is higher	99.92
SO_2	kg/hr (lb/hr)	< 627 (1381) (per air monitoring plan)	0.03 (0.069)	NA	NA	—	—	NA	NA
Particulate emissions[d]	mg/dscm (gr/dscf)	< 90 (0.04)	13 (0.0059)	180 (0.08)	36 (0.016)	22 (0.01)	4.5 (0.002)	180 (0.08)	5 (0.0022)
Carbon monoxide emission concentration[d]	ppm_{dv}^{d}	< 100	1	< 100	1.18	< 100	3.0	< 100	10.8
Total hydrocarbon (as propane) emission concentration[d]	ppm_{dv}	< 100	1.25	NA	NA	—	< 1.0	< 20	1.8
O_2 concentration in stack gases	% dry	> 3.0	9.9	NA	NA	> 3.0	11.6	NA	10.5
NO_x as NO_2 emissions	ppm_{dv} (kg/hr [lb/hr])	16,000 Max Calender Quarter mean[e]	91.7[f]	NA	6.1[g]	—	62.0	NA	287[f]
Visible emissions	% opacity	NA	NA	20	0	—	0	NA	NA
PCDD/PCDF, total	ng/dscm	< 30	< 1.24	NA	NA	—	—	NA	24.2
TCDD-TEQ	ng/dscm	NA	< 0.0288	NA	NA	—	—	NA	0.34
2,3,7,8-TCDD	ng/dscm	NA	NA	NA	NA	NA	NA	NA	NA

[a] Average for four runs.
[b] Average for two trains; average of three runs for each train.
[c] Average of Trial Burn Runs 6, 7, and 8.
[d] Corrected to 7% oxygen.
[e] Louisiana State ambient air quality standard.
[f] Oxygen burner-based system.
[g] Air-based system.
NA-Not available.

scrubber based APCS is shown in Figure 1. The HTTS®'s wet APCS is a modified venturi scrubber referred to as Tandem Nozzle Scrubber® manufactured by Hydrosonic® Systems. A continuous liquid purge is discharged from this unit. This liquid discharge is either disposed of in a nearby POTW, treated in an on-site WTS, or added to ash for cooling and conditioning.

Typical Process Flow Diagram for Dry and Dry-Wet APCS

A typical process flow diagram of the dry and dry-wet APCS for incinerators is shown in Figure 2. The system consists of a partial quench, a primary reactor such as a spray dryer or a dry reactor, a secondary reactor such as a baghouse or a dry electrostatic precipitator (ESP), and a sorbent slurry/powder injection system. The sorbents commonly used are hydrated lime ($Ca[OH]_2$), limestone (Ca_2CO_3), and sodium bicarbonate ($NaHCO_3$). The purposes of the partial quench are to reduce the gas temperature to thermally protect the baghouse and to increase the relative humidity of the gas which enhances the acid gas removal. The partial quench is sometimes not required if the APCS includes a boiler and the gases already contain large amounts of moisture. In cases where stringent acid gas standards are to be met, a polishing packed bed scrubber or wet electrostatic precipitator (WESP) may be included downstream of the secondary reactor. Sodium hydroxide (NaOH) is normally used in the polishing step device to neutralize traces of acid gases before the gases exit through the stack. The use of $NaHCO_3$ in the dry reactors may eliminate the need for additional polishing scrubber in some cases, but must be weighed against the operating cost of $NaHCO_3$ which is 3 to 4 times the cost per pound of acid gas removed when compared to $Ca(OH)_2$ and Ca_2CO_3. The dry solid by-product that is discharged for a dry or dry-wet APCS is normally landfilled on or off site.

Trends in Air Pollution Control Systems in Incineration Industry

Wet scrubbing systems have been traditionally used for removal of acid gases and particulate from incinerators. In

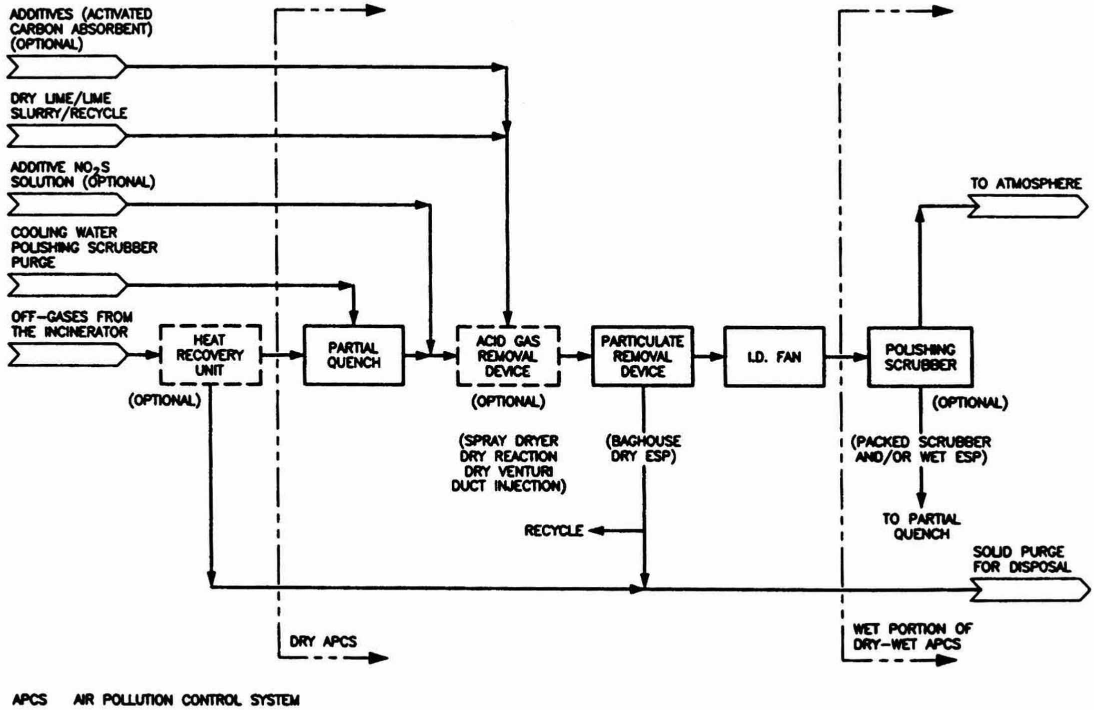

FIGURE 2 Block flow diagram of dry and dry-wet air pollution control system with optional enhancements.

1991, the EPA specified dry systems as the "Best Demonstrated Technology" (BDT) for municipal waste combustors (MWC), primarily due to the generally better particulate and metals removal efficiencies when compared to wet APCSs. However, acid gas removal by dry scrubbing systems is generally less efficient than wet systems, and due to De Novo synthesis dioxin/furan emissions can be higher. Medical waste incinerators (MWI), typically smaller units than MWCs, have followed the MWC industry by using dry APCSs. During the last 10 years, HWI in the United States which has typically used wet scrubbers are moving toward use of dry and dry-wet APCSs to meet more stringent emissions standards for particulate and metals. The European HWI industry has used dry and dry-wet systems for some time, to meet emission standards which are generally even more stringent than those in the United State (Acharya, P., Pakrasi, A., *et al.* [7]).

Process Challenges in the APCS

The two critical issues regarding the APCS are the higher removal efficiencies required for various pollutants in order to meet the increasingly stringent stack gas emission criteria, and the disposal of liquid and solids discharge from wet and dry systems, respectively.

The pollutants of concern are the particulate, acid gases including HCl, Cl_2, and sulfur oxides (SO_x), RCRA regulated metals, and dioxins/furans. The data for these pollutants in IT's wet system is presented in Table 2. The data includes the actual emission data compared with the site-specific ROD-driven criteria for Sikes and BB projects in which lightly contaminated soils are processed. This wet scrubber based data is then compared with dry system data from Chemical Waste Management's (CWM) incinerator deployed at Sauget, Illinois and CWM's transportable incinerator used at the Old Midland Superfund site of Ola, Arkansas.

The BB system consists of wet APCS with a full quench and a Tandem Nozzle Scrubber®. The Sikes system consisted of a dual train APCS with each of the train consisting of a quench and a Tandem Nozzle Scrubber®. CWM's Sauget system uses a single partial quench and a dual train APCS with each train consisting of a spray dryer/baghouse. CWM's Old Midland system was a single partial quench, two parallel baghouses (no spray dryer), venturi quench, and packed bed scrubber. It is evident from Table 2 that the wet APCS has met and, in many cases, far exceeded the stack gas criteria for each of the two sites. Available data on CWM's dry and dry-wet APCSs in Table 2 show that these units have also met or exceeded the required criteria.

APCS Enhancements

Incinerator operators are increasingly using enhancements to their systems to meet more stringent requirements. A common addition to either a dry or a wet APCS to improve particulate, metals, and dioxin/furan control is a wet electrostatic precipitator (WESP). A common addition to dry APCSs for better acid gas control is a packed bed scrubber. Another method to enhance removal of dioxins/furans is to inject activated carbon/coke upstream of the baghouse of a dry APCS or to install a carbon adsorber downstream of the scrubber in a wet APCS. Na_2S solution can also be injected upstream of the baghouse or

TABLE 3. Comparison of Trial Burn Data for the Dry APCS and Several Dry-Wet APCS at Savannah Army Depot, Northern Ohio, LaSalle Electric and Western North Carolina Projects

		Dry APCS		Dry-Wet APCS		Dry-Wet APCS		Dry-Wet APCS	
		Savannah Army Depot Project		Northern Ohio Project		LaSalle Electric Utilities Project		Western North Carolina Project	
Parameter	Units	Objective	Actual Emissions	Objective	Actual Emissions	Objective	Actual Emissions	Objective	Actual Emissions
Solid [liquid] feed rate	mtph (tph)	18.1 (20)	19.3 (21.3)	4.5 (5), [4 pgm]	4.9 (5.4), [2.7 gpm]	15.4 (17)	15.6 (17.2)	—	2.2 (2.5)
DRE = TNT (indigenous)	%	≥ 99.99	> 99.9998				—	—	—
DRE = PCB	%	—	—	≥ 99.9999	99.99995	≥ 99.9999	99.9999	—	—
DRE = Trichlorobenzene	%	—	—	≥ 99.99	99.9952	—	—	—	—
DRE = 1,1,2 TCE	%	—	—			—	—	—	—
DRE = Tetrachloroethene	%	—	—			—	—	—	—
						—	—	< 99.99	< 99.9995
HCl removal efficiency	% or kg/hr (lb/hr)	—	0.08 (0.176)	NA	0.13 (0.28)	> 99	> 99.996	> 99% or < 1.8 (4), whichever is greater	99.91 0.0087 (0.019)
SO_2	kg/hr (lb/hr)	NA	NA	NA	0.49 (1.07)	NA	NA	NA	NA
Particulate emissions[d]	mg/dscm (gr/dscf)	180 (0.08)	17.4 (0.0077)	NA	4.0 (0.0018)[c]	NA	3.75 (0.00167)	180 (0.08)	0.52 (0.0002)
Carbon monoxide emission concentration[d]	ppm_{dv}	NA	NA	NA	NA	NA	3.7	NA	NA
Total hydrocarbon (as propane) emission concentration[d]	ppm_{dv}	NA	NA	NA	NA	NA	0.2	NA	NA
O_2 concentration in stack gases	% dry	NA	NA	NA	5.2	NA	6.8	NA	NA
NO_x as NO_2 emissions	ppm_{dv} (kg/hr [lb/hr])	NA	NA	NA	NA	NA	NA	NA	
Visible emissions	% opacity	NA	NA	NA	NA	NA	NA	NA	NA
PCDD/PCDF, total	ng/dscm	NA	NA	NA	NA	NA	NA	NA	NA
TCDD-TEQ	ng/dscm	NA	NA	NA	NA	NA	NA	NA	NA
2,3,7,8-TCDD	ng/dscm	NA	NA	NA	NA	NA	3.3	NA	NA

[a] Feed rate of soils and non-pumpabale sludge.
[b] Feed rate of pumpable liquids (waste oil).
[c] Concentration corrected to 12 percent CO_2.
1,1,2 TCE-Trichloroethane.
NA-Not available.

with the lime slurry to enhance removal of mercury in a dry APCS. In a wet APCS, sub-cooling (sensible heat removal) of the combustion gases to approximately 125°F prior to passing the gases through a high energy scrubber or WESP will further improve particulate and metals removal.

Residuals Discharge From APCS

Organics and metals removed in the APCS will be transferred to the liquid or solid purge. At IT Superfund sites, the sludge from the HTTS®'s wet APCS was blended with the ash. At CAAP, the liquid purge from the wet APCS was also blended with the ash. At MOTCO, the liquid purge was piped to a POTW for treatment and disposal. On-site WTSs were used at LAAP, Sikes and BB sites to treat liquid purge from the APCS because no POTWs were available. The solids purge from dry systems are normally handled in accordance with the ROD criteria for the soils, usually landfilled on site. If the organic levels in the solids purge are unacceptable, the solids can be retreated in thermal treatment system. If metals levels in the solids purge are unacceptable, the solids may require stabilization and/or disposal in an off-site, secure landfill. For dry-wet APCSs, the liquid purge is normally reinjected in the partial quench for combustion gas cooling and the resulting solids are captured in the baghouse. The liquid purge from a dry-wet APCSs may also be blended with the ash. Clearly, the trend is towards zero-liquid discharge and, therefore, dry or wet-dry APCS may be preferred or even specified by some clients.

Plume Suppression Systems

The primary reason for a plume suppression system (PSS) is aesthetics. The use of PSS, particularly for such combustion sources as fixed facility HWIs, is increasing in the United States. In the absence of a PSS, the moisture in the off-gas from the APCS of a combustion device usually produces a visible water vapor plume as it mixes with the ambient air and can be misinterpreted by the public as pollution. Most of the steam plume moisture comes from the gas cooling step the following combustion zone.

A visible moisture plume is formed when the water vapor in the stack gas is cooled to saturation by mixing with ambient air to form suspended water droplets. The visibility of the plume is dependent upon the density of the water droplets. Plume suppression involves controlling the humidity and temperature of the combustion gas such that either the saturation is not reached upon mixing with ambient air, or if saturation does occur, the water droplets are sufficiently dispersed so as to not be visible.

In the most efficient PSS design, the steam plume is suppressed by first removing most of the water vapor from the stack gases by using a condenser and then adding heated dilution air to the off-gas at the stack. The typical condensing equipment includes a water cooled heat exchanger for removing sensible heat from the combustion gas and condensing water vapor. A steam or combustion gas heated heat exchanger is used to heat ambient air. The heated ambient air is then added to the cooled combustion gas in the stack. The heated air increases the combustion gas temperature and dilutes its moisture content, thus eliminating or reducing the visible moisture plume as the combustion gas mixes with ambient air (Acharya, Kirslis, S., *et al.* 1994). Most incinerators deployed in Superfund sites do not have PSSs, however, PSSs are mandatory in many European countries.

The operating cost of the PSS is relatively high. In order to minimize such costs, it is critical that the design basis be well defined prior to the design of the PSS. The design basis includes the desired degree of plume suppression and properly selected design ambient conditions (temperature and humidity) (Acharya, Kirslis, S., *et al.*, [8]).

SUMMARY AND CONCLUSIONS

The following summary and conclusions are based on IT's experience in soil remediation projects and on data and information from others in the industry.

The system capacity (tons/hr) is the key contributor to the overall project economics. A proven method of increasing the capacity in fixed system without increasing equipment size is to utilize an oxygen-based combustion system which can even be retrofitted to an existing system.

Infiltration air into the kiln has an adverse impact on the processing capacity, induced draft fan capacity and may produce higher NO_4 emissions in systems using oxygen-burners. The suspected infiltration locations should be regularly tightened and feed/ash systems selected to minimize leakage.

"Solid residence time at temperature" relationship is the key to meeting ash criteria for organics. It is recommended that the "time at temperature" relationship be developed for each project, at least through bench-scale tests, to determine the proper rotary kiln operating temperature and solids retention time and thereby avoid expensive ash reburn.

The keys to estimating metal emissions in the stack gases is in the selection of accurate system removal efficiencies. These data can be obtained from several sources including trial burn data and research studies conducted at various EPA laboratories.

Particulate carry-over for sandy soils is 7 to 10 percent of wet feed rate. Particulate carry-over can be as low as 2 percent if silty soils are blended with clay under certain conditions.

Relatively inexpensive, bench-scale ash slagging potential tests can help predict slagging potential of a particular soil matrix in a given system. Once the slagging potential is determined, appropriate system design and/or operational changes can be made, if necessary, to avoid or control slagging.

Available data indicates that if the SCC incineration temperature is maintained higher than 1600°F, at a typical residence time of 2.0 seconds, all but trace organics including dioxins/furans are essentially destroyed if there is adequate air/fuel mixing and excess oxygen. These conditions will minimize combustion-related emissions such as CO, THC, POHCs, and dioxins/furans.

APCS design is constantly undergoing improvements to meet the changing particulate, acid gases, metals, and dioxins/furans emissions performance, and plume suppression requirements. Usually, additional equipment installation and process conditions changes are required to meet more stringent emissions requirements. The regulatory trend is toward zero-liquid discharge from HWIs, forcing the thermal remediation industry to install dry or dry-wet APCSs that discharge solid by-products and, compared to wet scrubbers, have better removal efficiencies for some pollutants.

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Removing a Small Quantity of THT from Gas Storage Groundwater Through Air Stripping and Gas-Phase Carbon Adsorption

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This paper deals with the response to a case of contaminated groundwater located in France. The natural gas is stored during summer in porous underground rocks. When energy requirements increase (particularly in winter), gas is drawn off, but water is also pumped during this operation. The water has a strong characteristic odour of the TetraHydroThiophene (THT), which has been used by Gaz de France as an additive in order to detect gas leakages because of its strong odour. Unfortunately, the presence of THT in medium other than natural gas can be responsible for safety problems. Gas stripping combined with adsorption on granular activated carbon was chosen to obtain removal of THT from the groundwater. The gas to water ratio for stripping column is higher than usual and the gas used for stripping was recycled in order to prevent air pollution. Carbon consumption is approximately 3 tons a year.

INTRODUCTION

Recently, reports of cases of contaminated groundwater have increased and concern for groundwater quality has become a major environmental issue. More and more demands will be placed on the chemical engineering profession to prevent and respond to such contamination. This paper deals with the response to one case of contaminated groundwater in France. Gaz de France (GdF) is the firm which is responsible for the storage, transportation and distribution of natural gas in France.

The gas imported by GdF from foreign countries is stored during summer in porous underground rocks. The gas injected under pressure takes the place of the water primary located in these rocks. When the energy requirements increase (particularly in winter), gas is drawn off, but water is also pumped. This water has the characteristic odour of the TetraHydroThiophene (THT). THT is used by GdF as an additive in order to allow gas leakages detection, because of its strong odour at concentration above 1 ppb, which is the detection limit. Unfortunately the presence of THT in another compound than natural gas can be responsible for safety problems. Consequently, removing THT from groundwater is a major problem for GdF.

GdF process currently used to get rid off the molecule of THT is efficient, but very costly. A feasibility study was started to find a less expensive way to treat the contaminated water. Based on trends observed on the site, standard concentration for THT in the effluent is about 20 mg/L.

Water treatment must be very efficient because water containing more than 0.5 mg/L of THT has an odour. Three treatment methods were considered: air stripping, diffused aeration and adsorption on Granular Activated Carbon (GAC). Diffused aeration was first investigated for its ability to prevent any fouling of the air stripping column, but results have shown that this method is not sufficiently efficient in removing contaminant. Ruggiero D. [*1*] has shown that packed tower air stripping is much more efficient than diffused aeration for removing Volatile Organic Compounds (VOCs) from water. Consequently, packed tower air stripping was investigated and found to be acceptable. Packed tower air stripping is also in this case a more suitable method than diffused aeration.

The choice between packed tower air stripping and GAC adsorption depends on the compounds involved, the expected effluent concentrations and the treatment objectives [*2*]. A preliminary study of GAC adsorption was performed in the laboratory. The results indicated that adsorption was not efficient due to small amounts of bituminous compounds from additional water mixing with the main effluent (see below) obstructing the carbon sites. Consequently, packed tower air stripping was selected for the treatment process.

In the air stripping operation, THT is transferred from the liquid phase into the air phase thus creating an air pollution problem. Thus, off-gas treatment is required. Available off-gas treatment technologies include vapour phase GAC adsorption, catalytic incineration and UV-ozonation. GAC adsorption is the most common air emissions control process and is generally more cost effective than alternative methods such as incineration. This latter requires large amounts of energy for the high temperature combustion of the off-gases, and may result in emissions control costs that are two to three times higher than the cost of treatment with

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vapour phase GAC [3]. Consequently, gas adsorption on Granular Activated Carbon was investigated.

GAC adsorption is a well established technology for removing organic compounds from vapours and has commonly been used with success in odour control [4]. Moreover, the use of air stripping prior to carbon adsorption has advantages because the reduction of VOCs over activated carbon treatment decreases the consumption of GAC by reducing the contaminants for which carbon has a lower capacity. Due to the environmental impact of THT, the air used for the stripping column has to be treated by a subsequent GAC adsorption column, which objective is to fix the THT. Thus the air is used in a circulation loop with only a small external air introduction in order to control the pressure of the installation.

STRIPPING

For most VOCs, sufficient data are available in the literature to allow one to design an air stripping tower without undertaking a pilot study. However data for THT are not available in the literature. Moreover, the groundwater is mixed with water from another industrial unit, which contains small amounts of bituminous compounds, other VOCs and approximately 20 g of methanol per liter. For this reason, a pilot unit was built and an air stripping study was carried out.

Pilot Unit and Test Procedure

An air stripping pilot column was set up and operated. The purpose of the pilot study was:

- To determine if high removal efficiencies could be achieved for THT
- To validate a model in order to provide guidance in sizing the full scale plant.

A 30-cm diameter glass column was tested (Fig. 1). The feed was liquid effluent from gas pumped into the underground GdF site. Preliminary diffused aeration study had been performed with the same column. Major features of the set-up are noted below:

- 30-cm diameter glass pipe column
- 1 meter packing of 15 mm PVC pall rings
- air supply-compressed air flow measured by a rotameter
- tap water supply
- water stored in a cover tank and pumped to column through a rotameter.

The mass transfer performance of the air stripper was determined by taking samples of the contaminated water both at the inlet and at the outlet of the column. For each run, the air and water flow rates were set to the desired rotameter readings. THT inlet concentration varied from 12 to 40 mg/L with an average value between 25 and 30 mg/L. The average concentration obtained during each test was the value reported for each experiment. Water samples were analyzed using a gas chromatograph with a FID detector for methanol and with a special detector made by GdF for THT.

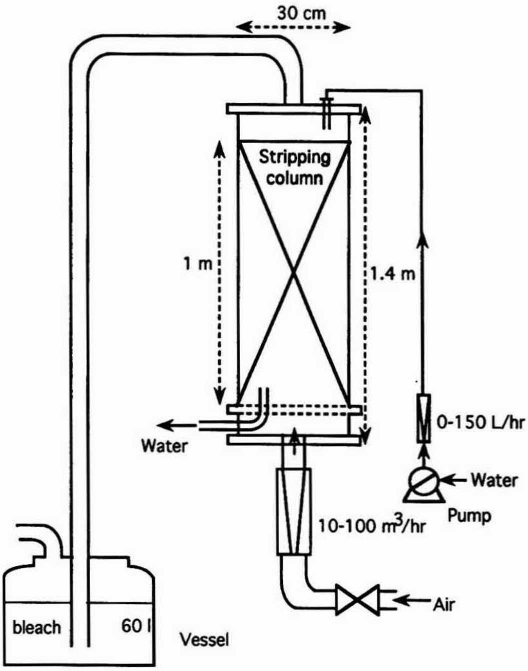

FIGURE 1 Sketch of the air stripping pilot unit.

Process Model

An air stripping model has been established to evaluate THT results. The mass transfer model was based on a two-phase resistance approach using Mersmann and Dexler correlations [5]. This model was used to determine liquid and gas phase mass transfer coefficients; these data were then used in the design of the air stripping process.

Air stripping of THT was expected to behave like a classical dilute solution [6]. Such applications are characterized by straight line equilibrium relationships and straight operating lines, which allow some mathematical simplifications compared to the most general case:

$$Y_A = HeX_A \qquad (1)$$

where:

X_A = concentration of component A in the liquid phase (mol/m^3)
Y_A = concentration of component A in the gas phase (mol/m^3)
He = Henry's law coefficient

The rate of mass transfer across an air-water interface for the stripping process is controlled by the sum of the resistance of the liquid and gas phase boundary layers [6]. Assuming that Henry's law describes the chemical equilibrium conditions between the air and water phase, the overall rate constant k_L is given by:

$$k_L a_e = \left(\frac{1}{\beta_L a_e} + \frac{1}{\beta_G a_e H_e} \right)^{-1} \qquad (2)$$

in which:

k_L is the overall mass transfer coefficient (m/s)
β_L is the mass transfer coefficient for the liquid phase (m/s)
β_G is the mass transfer coefficient for the gas phase (m/s)
a_e the specific area of the packing (m^2/m^3).

Note that the product $k_L a_e$ is equivalent to the first order mass transfer rate constant. The values of β_L, β_G and a_e in Equation (2) are respectively determined by the correlations (3), (4) and (6) developed by Mersmann and Deixler [5]:

$$\beta_G = K_G \left(\frac{w_G^2 D_G^2}{d_N \nu_G} \right)^{1/3} \tag{3}$$

$$\beta_L = 0.86 \left(\frac{6 D_L}{\pi d_N} \right)^{1/2} \left(\frac{w_L^{1.2} g^{1.3} \sigma_L^{0.3} \psi^{1.2} (1 - 0.93 \cos \theta)^2}{\nu_L^{1.4} \rho_L^{0.3} a_t^{2.4}} \right)^{1/6} \tag{4}$$

$$a_w = 3.49 w_L^{0.4} \nu_1^{0.2} \left(\frac{\rho_L}{\sigma_1 g} \right)^{0.15} (1 - 0.93 \cos \theta)^{-1} \left(\frac{a_t^2}{4 \pi \psi} \right)^{0.6} \tag{5}$$

$$a_e = F a_w \tag{6}$$

in which:

a_t is the surface area per unit volume of packing (m^2/m^3)
a_w is the wet surface area per unit volume of packing (m^2/m^3)
D_G is the gas phase diffusion coefficient (m^2/s)
D_L is the liquid phase diffusion coefficient (m^2/s)
d_N is the nominal size of packing element (m)
g is the gravitational acceleration (m/s^2)
K_G is a coefficient which depends of the shape of the packing
w_G is the superficial gas velocity (m/s)
w_L is the superficial liquid velocity (m/s)
θ is the contact angle (degree)
ν_G is the kinematic viscosity of gas (m^2/s)
ν_L is the kinematic viscosity of liquid (m^2/s)
ρ_L is the density of liquid (kg/m^3)
ρ_G is the density of gas (kg/m^3)
ψ is the void fraction of packing (−).

The application of mass transfer relationships to the design of packed towers is well understood and documented in the chemical engineering literature [6, 7]. For a dilute solution, a relationship is derived relating the fraction of the contaminant remaining in the effluent to the Number of Transfer Units (NTU) in the column and the stripping factor:

$$NTU = \frac{S}{S-1} \ln \left(\frac{(C_{IN}/C_{OUT})(S-1)+1}{S} \right) \tag{7}$$

$$(\mathrm{HTU}) = \frac{w_1}{k_L a_e} \tag{8}$$

$$Z = \mathrm{HTU} * \mathrm{NTU} \tag{9}$$

in which:

NTU is the Number of overall liquid phase Transfer Units
HTU is the Height of Transfer Unit (m)
C_{IN} is the inlet concentration of pollutant (mol/m^3)
C_{OUT} is the outlet concentration of pollutant (mol/m^3)
S is the stripping factor : $He\ G/L$ (−).

The performance of air stripping is temperature dependent and thus the liquid and gas phase parameters used in this model must be adjusted to the contaminated water and gas temperature conditions expected during treatment. To provide a performance safety factor for final design, it may be appropriate to adjust all model parameters to the lowest temperature expected: 10°C is representative of the normal winter groundwater and ambient air temperature at the site. Henry's law coefficient *He* is not available for THT. Consequently, *He* is an unknown parameter in the designed equations; it will be optimized to fit the experimental results. Diffusivity coefficients were calculated using theoretical and empirical correlations from literature [7, 8].

The pilot study has been performed to confirm the correct selections of parameters used in the model, then to validate it in order to design the industrial column. A large range of air and water flow rates were tested. Volumetric air to water ratios ranged from 170 to 1200, which is larger than usually found in the literature, because a high THT removal is required without increasing too much the size of the tower. Moreover, the operating temperature is low (10 to 14°C), which increases the difficulty to strip. Pilot test-run results are presented in Table 1.

The average inlet concentration of THT on site is 25 mg/L and the required outlet concentration is about 0.5 mg/L, thus the required efficiency of THT removal is 98%. Experimental results confirm that, if the size of the tower is small, a very high G/L ratio is required to achieve a THT removal of 98%. Consequently, a value of G/L of about 1000 was selected for the industrial stripping column.

In order to use the model to simulate experimental results, it was necessary to fit Henry's law coefficient *He*. HTU and NTU depend on *He*, and the height of packing Z is 1 meter. Equation (9) enables one to calculate the value of *He* which fits experimental results. Taking $He = 4.5\ 10^{-3}$, experimental results are well described by the model. Figure 2 illustrates the proportion of THT removal for both ex-

TABLE 1. Pilot test-runs giving the THT concentration in the outlet effluent versus the THT concentration in the inlet effluent for different operating conditions

Experiment #	1	2	3	4	5	6	7	8
Air flow G (m3/hr)	25	25	25	25	25	45	25	60
Water flow L (L/hr)	150	120	100	80	60	60	30	70
G/L ratio	167	208	250	312	417	750	833	1167
C_{IN} (mg/L)	31	32.5	32.5	33.5	33	28	32.5	25
C_{OUT} (mg/L)	6.2	5.5	3	2.5	2	0.5	1	0.5

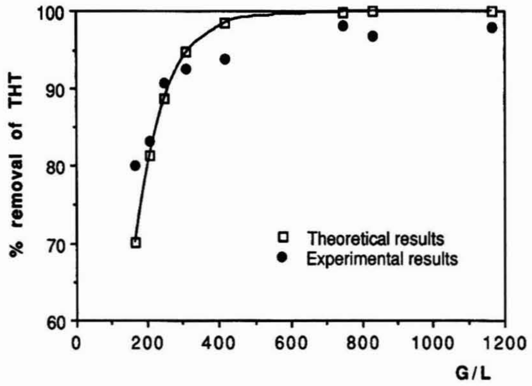

FIGURE 2 Comparaison between theoretical and experimental proportion of THT removal during the air stripping process.

perimental results and model predictions. So, the model provides a reliable method to design the industrial column.

For ratio G/L around 1000, results are fitted well with $He = 1.7\ 10^{-3}$. As this ratio G/L has been selected for the industrial column, it seems better to take the lowest value of *He* to design the industrial column in order to provide a safety factor in the design. Pilot test runs have shown that most of the VOCs compound are easier stripped than THT. On the contrary, only 5 to 10% of methanol is stripped, whatever the air to water ratio and whatever the methanol concentration. So methanol will have to be removed by another process, e.g., biological.

The model developed has been used to calculate the following industrial installation:

Height of packing	3.7 m
Column diameter	1 m
Liquid flow rate	1 m^3/hr
Gas flow rate	1000 m^3/hr

Air stripping should achieve 98% removal of THT from the liquid and the effluent should contain acceptable THT concentration. The VOCs are also removed in the gas phase and their outlet water concentration is below limits. Since the methanol is not totally stripped, the effluent will have to be biologically treated.

GAC ADSORPTION

The first decision in using Granular Activated Carbon (GAC) adsorption is normally a choice between a regenerable and a nonregenerable system. The initial capital expenditure for regenerable system combined with expenses for utilities to operate this system are often greater than the expenses of replacing carbon for a nonregenerable system [*4*]. GdF now uses GAC in a desulfuration process at Cerville plant and approximately 8 tons per year of spent carbon are treated by a specialized company. Consequently, if the quantity of activated carbon from adsorption process is not too high (a few tons a year), it will be possible to treat the spent carbon in the same way. Consequently, a nonregenerable system was investigated.

In a nonregenerable system, the contaminated air from the air stripper is passed through either one or two vessels containing GAC and then discharged to the atmosphere. After a period of time when the carbon is exhausted and impurities began to break through, the carbon is replaced with fresh virgin carbon.

The air stripping column design has shown that a high gas flow rate is necessary, the gas will be recycled in order to prevent air pollution. However, the methanol is not removed during the stripping and it will be necessary to investigate the water-methanol-air equilibrium. It is known that the explosive level is reached for a given percentage of methanol in air at equilibrium (between 6 and 36% methanol in air). A preliminary estimation shows that the percentage of methyl alcohol in the gas phase is very low. As a consequence, it is not necessary to use nitrogen instead of air to prevent the risk of explosion. This is fortunate because of the very high cost that would be incurred by use of nitrogen.

Thus, our purpose was to study the adsorption of the different pollutants: methanol, THT and all other contaminants contained in the air stream. Most of the research to date concerned adsorption of single organic components on fresh carbon at low contaminant concentrations. Moreover, no information on THT is available in the literature and the theoretical derivations for multicomponents systems are complex and difficult to use. Therefore, the problem is more complicated because concentrations of THT are approximately a few micrograms per liter whereas concentration of methanol is in the grams per liter range. Consequently, methanol can rapidly saturate all the activated sites of the carbon. Knowing that activated carbon has more affinity for larger molecules with a double bond, we can expect that methanol will desorb whereas THT will adsorb. Another problem occurs because the air stream will be saturated with water; consequently the capacity of carbon will be less than expected. To alleviate this problem partially, the relative humidity of the gas was reduced by passing the gas through an electrical heater.

The design of the full-scale carbon adsorption system, which is sometimes based on theoretical predictions will come from a pilot study and from "rules of thumb" factors and past operating experience. Our purpose for the pilot study was to see if THT is efficiently adsorbed by granular carbon and to provide data for the design of the industrial adsorber. The sketch of the gas phase adsorption pilot is shown on Figure 3 and major features of the unit are listed below:

- Stripping column: 5 cm diameter glass pipe, 1.8 m packing
- Compressor and pump
- Adsorber: 10 cm diameter glass pipe
- Electrical heater

The temperature of both inlet and outlet water was measured before the stripping column as well as in the adsorber. Water samples were taken in the inlet and outlet water to determine the total amount of contaminants removed in order to calculate the breakthrough time of the carbon bed. However, it must be reminded that the main purpose of the process is to remove THT from the effluent, the VOCs future being not considered too much disturbing because they can be treated in an open air wastewater treatment plant. Testing was done using water spiked to approximate the projected effluent concentrations at Cerville (Table 1). Volumetric gas to water flow rates were

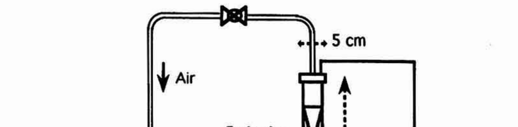

FIGURE 3 Sketch of the pilot unit combining air stripping and GAC adsorption.

maintained at constant values during the stripping column pilot study. Tests were operated with water at room temperature. The impact of relative humidity was investigated by heating the off-gas from the stripper at three temperatures T_g (20°C, 35°C, 55°C).

Two different heights of carbon bed were studied: $H =$ 10 cm and $H =$ 20 cm. It was necessary to work with such heights to ensure that the adsorption wave can be well established, because no predictions were possible concerning its length. Consequently, experiments are carried out during up to 15 days to reach the breakthrough point. The carbon bed is considered to be saturated when the THT concentration in the outlet water stream began to rise: the corresponding time is the breakthrough time. Breakthrough curves for a carbon height of $H =$ 10 cm and at the three different temperatures T_g are illustrated in Figure 4. Table 2 shows the breakthrough time and carbon usage rate for $T_g =$ 20°C, 35°C, 55°C with $H =$ 10 cm and $H =$ 20cm.

With gas preheated to 20°C, the carbon ageing rate is approximately ten times higher than if the gas is preheated to 35°C. On the other hand, preheating the gas to 55°C instead of 35°C induces a slight increase of the carbon usage rate. The impact of relative humidity explains the results on THT adsorption. At high relative humidity values (i.e. $T_g =$ 20°C), most of the granular activated carbon pores are filled with water and the adsorption capacity is very low. But, if the relative humidity is lowered below 40% (i.e. $T_g =$ 35°C), the adsorption capacity increases significantly due to much more dried pores. Stenzel and Gupta [*4*] noticed that the carbon life can be extended, and therefore the carbon usage can be lowered by a factor of three to four by lowering the relative humidity of the air stream to less than 40%. As soon as the pores become drier, further heating reduces the capacity and the carbon consumption is slightly higher for $T_g =$ 55°C than for $T_g =$ 35°C. Therefore, the recommended gas temperature (T_g) will be 35°C, which corresponds to a carbon usage rate of 43 g carbon/g THT.

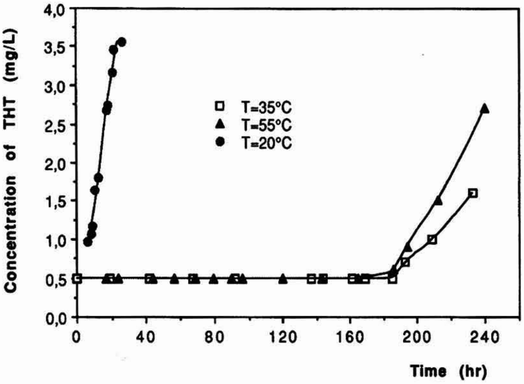

FIGURE 4 Breakthrough curves of THT for a carbon bed height of 10 cm at three different gas temperatures.

Results also showed that the methanol concentration is kept constant in the outlet water streams for all the cases studied, whereas air stripping study has shown a 5% to 10% removal of methanol in the stripping column. In fact, the methanol single adsorption isotherm capacity is high, which means that the methanol is probably adsorbed first and desorbed second when the THT adsorption wave is established in the carbon bed. In a multicomponents vapour stream, competitive adsorption takes place and the adsorption capacities are usually lower than single component isotherm capacities. The equilibrium air-methanol-water is achieved in the column. As mentioned in the stripping study, methanol will have to be biologically treated.

GdF site is required to treat 2700 m^3 of contaminated groundwater per year (containing about 54 kg THT) which results in a carbon usage of 2.3 tons a year. Three tons a year might be considered to ensure a conservative design. Thus, the company which is already in charge of the treatment of the 8 tons of spent activated carbon from Cerville will be able to treat the extra 3 tons by the same time.

The simple linear relation established between the height of carbon bed and breakthrough time of the carbon bed enables to propose design specifications for the adsorber:

- Height of carbon bed: 1.5 m
- Diameter: 2.2 m

TABLE 2. Breakthrough time and carbon usage rate for different temperatures and two different heights of carbon bed

Height of carbon bed(cm)	10	20
Breakthrough time (hr)	15 (20°C) 190 (35°C) 175 (55°C)	44 (20°C) 380 (35°C) 350 (55°C)
Carbon usage rate (g carbon/g THT)	500 (20°C) 43 (35°C) 47 (55°C)	384 (20°C) 43 (35°C) 46 (55°C)

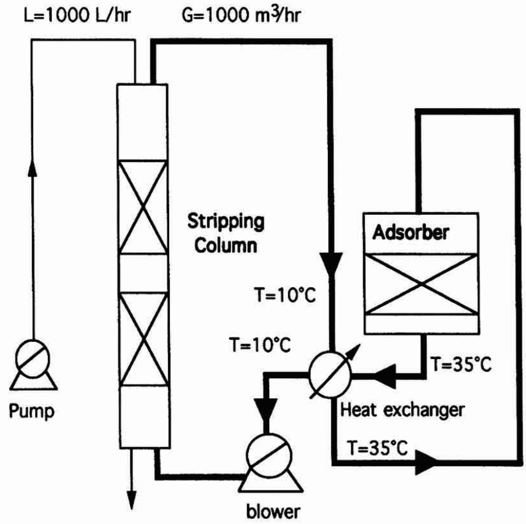

FIGURE 5 Sketch of the industrial full-scale installation combining air stripping and GAC adsorption.

Note also that the gas velocity in the adsorber is below the value of 100 m/min which is the limited value usually acceptable for this kind of adsorber.

FULL-SCALE INSTALLATION

The full-scale installation combining air stripping and GAC adsorption is sketched in Figure 5. It has been effectively built on the Cerville site and contains the following features:

- Stripping column 1-m diameter: 3.7-m height of packing
- Air flow rate 1000 m^3/hr
- Liquid flow rate 1 m^3/hr
- Adsorber: 1.5-m height, 2.2-m diameter packing
- Heat exchanger to preheat air at 35°C before entering adsorber
- Compressor for the air flow rate
- Pump for the groundwater extractor

As this installation has been operating during just one winter season, the first studies have been devoted to the optimization of its behaviour through variations of some major parameters. Because of the industrial constraint, only the operating conditions which are supposed to get rid of most of the THT has been tested. In general, the yield of THT stripping has confirmed the pilote results in spite of important concentration fluctuations in the inlet effluent. An accurate cost study is now too early however, the promises are good and expectations should be confirmed.

CONCLUSION

Air stripping combined with GAC adsorption is an efficient technology for cleaning groundwater contaminated by VOCs and THT. A sufficiently high removal of THT from the groundwater is achieved by gas stripping to prevent any odour problem. The resulting THT contained in the off-gas is efficiently adsorbed by GAC. Carbon consumption is projected to be 3 tons a year, which is low enough compared to the 8 tons a year already used at the site. The gas to water ratio for stripping column is higher than usual and the gas used for stripping was recycled in order to prevent air pollution. The VOCs are also stripped in the air stripping column and adsorbed in the granular activated carbon bed. On the other hand, methanol also contained in contaminated groundwater is not removed in the stripper and will have to be biologically treated.

A first cost analysis has shown that the total cost of this process could be at least two or three times lower than the total cost of the process, which is currently used at Cerville. Moreover, as safety is a major problem in a gas site, the operating conditions of the process prevent any risks: it works at atmospheric pressure, with a low temperature of 35°C and because of the very low level of methanol in the gas phase, air can be used instead of nitrogen without any explosion risks.

ACKNOWLEDGMENTS

This work was carried out with the support of GdF (Gaz de France), whose help is greatly acknowledged. We would like to thank Mr. Sabbot-Durand, Mr. Simonin, Mr. Fillinger, Mr. Gobe and Mr. Paquet for their assistance during this study.

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Solid Waste Remediation in the Metallurgical Industry: Application and Environmental Impact

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This paper describes problems associated with the remediation of solid metallurgical wastes generated during primary manufacture of major metals (iron, copper, aluminum, zinc and lead). It focuses on three types of solid wastes: slags, dusts and sludges.

It has been shown that solid waste remediation technologies, such as stabilization or solidification, incineration, and hydro-chemical metal recovery, have been applied in the industry and new technologies such as plasma- and vitrification-processing of solid wastes are under development. On the whole, however, solid residue remediation remains relatively uncommon. In addition, currently applied technologies are unable to solve the complex problems of metallurgical solid wastes (e.g., simultaneous destruction of toxins and extraction of multiple metals).

A new thermal process applicable to direct ironmaking that would achieve significant utilization of zinc residues has been proposed. It has been suggested that the high-temperature treatment of wastes in which metallurgical furnaces are used as remediation reactors holds great potential as an alternative disposal method.

INTRODUCTION

The metallurgical industry is one of the major pillars of world industry. It is also one of the largest sources of environmental pollution. Every year it produces large quantities of gas, liquid and solid wastes. Worldwide production of four metals—aluminum, iron, copper and zinc—accounts for about 2,000 megatonnes of waste generated per year. Table 1 [*1*] indicates estimates of total emissions from metal processing operations. If discarded directly into the natural environment, such wastes would not only occupy enormous amounts of land, but also pollute air, soil and groundwater. Clearly, successful remediation efforts would greatly reduce the environmental impact.

An allied environmental concern is the gradual depletion of nonrenewable mineral resources as metal production steadily rises. Public demand for conservation of natural resources and their most suitable utilization, as well as for generation of the least possible waste, its reuse wherever possible, and proper disposal, is growing. Legislation defining standards for protection of the environment, first enacted in the metallurgical industry during the 1960s, has become increasingly stringent.

One of the most important challenges before the metallurgical industry, therefore, is to meet to exceed these requirements while maintaining or increasing productivity. Substantial research has been carried out to identify waste emissions from metallurgical processes and develop measures for their reduction [*2*]. Significant achievements have been made, notably the recycling of wastewater and the widely adopted practice of using SO_2 emitted during metallurgical operations such as copper and lead smelting to generate sulfuric acid for further industrial use [*3*].

However, many problems remain to be resolved. While many measures already exist to deal with waste gases, the remediation of solid metallurgical wastes demands new scientific advances. These wastes present a twofold challenge. Firstly, they are generated in such large quantities that metallurgical operations need to be optimized and new remediation techniques developed to substantially reduce their volume, mass and toxicity.

Secondly, the complex properties of solid wastes present particular difficulties for remediation efforts. As one example, dusts generated by steelmaking processes may contain varying amounts of iron, as well as toxic metals (zinc, lead, chromium, etc.). While current techniques are successfully treating some of these elements singly, no integrated methods have yet been industrially applied whereby the various associations of these substances which typically occur in solid wastes can be treated in a single and therefore cost-effective process.

Four basic principles [*4, 5, 6*] need to be applied in the remediation of solid wastes: reduction of waste generated, recycling of wastes, generation of valuable co-products, and treatment before landfill. Procedures for their implementation are detailed in Table 2. Application of these four principles could result in the conversion of wastes to useful products, their reduction or even their elimination. This would be a big step toward the most optimal use of mineral resources.

This article describes problems of the remediation of solid metallurgical wastes generated during primary manufacture of major metals (iron, copper, aluminum, zinc and lead) in recent years and the research results obtained. The solid waste streams and major remediation techniques are characterized. Areas requiring further investigation are

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TABLE 1. Total Emissions in Metals Processing

Emission	kg/T of metal				MT/Year			
	Al	Steel	Cu	Zn(Electrol.)	Al	Steel	Cu	Zn(Electrol.)
Carbon Dioxide								
Ancillary	7,814	486	5,124	3,589	142.3	373.1	56.7	25.48
Excl.Electricity*	4,500	1,085	2,051	NEA	81.9	833.0	22.7	NEA
Carbon Monoxide								
Ancillary	2	0.1	2.54	1.78	0.04	0.1	0.0281	0.0126
Excl.Electricity*	340	54.9	NEA	P	6.19	42.1	NEA	P
Sulfur Oxides								
Ancillary	58	3.5	37	26	1.06	2.69	0.41	0.1846
Excl.Electricity*	25	5.5	3,500	P	0.46	4.22	38.75	P
Nitrogen Oxides								
Ancillary	21	1.9	20	14	0.38	1.44	0.22	0.0994
Excl.Electricity*	2	1.1	NEA	NEA	0.04	0.87	NEA	NEA
Hydrogen Fluorides								
Ancillary	NEA	NEA	NEA	NEA	NEA	NEA	NEA	NEA
Excl.Electricity*	5	NEA	NEA	NEA	0.09	NEA	NEA	NEA
Liquid Effluents								
Ancillary	833	267	2,820	1,974	15	205	31	14.01
Excl.Electricity*	8,001	39,285	1,350,000	442	145	30,159	14,945	3.14
Solid Waste								
Ancillary	3,401	103	1,100	765	62	79	12	5.43
Excl.Electricity*	2,000	484	138,000	P	36	372	1,528	P

NEA—No estimate available; P--Present

*Values in these rows exclude the environmental impact associated with electricity production

TABLE 2. Remediation Principles for Solid Metallurgical Wastes

Principles	Procedures
Reduce generation	• Substitute less toxic and better-quality raw materials for those currently used • Institute methods that reduce waste by improving the efficiency of existing processing operations • Develop new production methods that limit harm to the environment
Recycle wastes	• Recover valuable elements from waste • Reclaim metal scrap • Use wastes to treat wastes • Use combustible wastes as fuel substitutes to generate energy
Generate co-products	• Reuse metallurgical wastes in other industries • Increase the extraction of multiple metals from wastes
Treat before landfill	• Segregate wastes according to their characteristics (e.g., hazardous or nonhazardous). "Delist" wastes are nontoxic wastes. • Treat wastes to reduce their volume, mass and toxicity

identified and future trends are described. Both the technological and environmental challenges and solutions are considered.

SLAGS

In pyrometallurgical smelting operation of metal extraction, the impurities (nonextracting elements) of raw ore with other materials form melting slag which can improve operation conditions of smelting furnaces, and influence the quality of extracted metal. When this melting slag is discharged and cooled, large amounts of waste slag are generated. These slags from pyrometallurgical industries are generally composed of CaO, SiO_2, FeO and other oxides. Typical components of selected slags resulting from the manufacture of primary metal are listed in Table 3 [7]. These slags have relatively stable physical and chemical properties after undergoing high-temperature processing. They may be air-cooled, water-cooled, granulated, expanded, or undergo other forms of treatments. According to demand, and depending on factory conditions, different properties and sizes of slags for use in various fields can be obtained. Table 4 shows some possible uses for metallurgical slags [*2, 8, 9, 10, 11, 12*].

TABLE 3. Main Components of Metallurgical Slags (%)

Component		CaO	SiO_2	Al_2O_3	MgO	MnO	P_2O_5	Fe*	CaO_{Free}	ZnO	Cu	Pb
BF	Slag	36–45	33–42	10–16	3–16	< 2	na	< 1	na**	--	--	--
BOF	Slag	42–55	12–18	< 3	< 8	< 5	< 2	14–20	< 10	--	--	--
EAF	Slag	25–40	10–17	4–7	4–15	< 6	< 1.5	18–29	< 3	--	--	--
RF	Slag	4–20	35–42	2–13	1–5	--	--	23–35	--	--	< 1	1–3
PbBF	Slag	5–20	19–35	3–8	3–5	--	--	21–28	--	5–25	< 0.5	< 1

TABLE 4. Applications of Metallurgical Slags

Slag	Facility	Quantity (T/T of metal)	Possible Uses
Ironmaking	Blast furnace	0.6 ~ 0.7	Raw material for cement production Railroad ballast Aggregate road building material Soil conditioning materials Mineral slag wool Porous aggregates for lightweight concrete
Steelmaking	Basic Oxygen Furnace Electric Arc Furnace	0.3 ~ 0.5	Reuse in metallurgical processes Fertilizer and lime Bulk materials Civil engineering
Coppermaking Leadmaking	Reverberatory Furnace Blast Furnace	2 ~ 4	Civil engineering Bulk materials Mineral slag wool Stone casting Source for recovery valuable metals

An ironmaking slag can be fully reused. However, there are still problems need to be resolved before the steelmaking and nonferrous slags could be used in a large scale. Thus, this paper focus on the remediation of these two types of slags.

Steelmaking Slags

Steelmaking slags can be recycled either by selection according to their composition for reuse in the steelmaking process in sinter plants or, given their high CaO content, by direct charge into blast furnaces as a lime agent.

The biggest field for new steelmaking slag applications remains construction. In recent years, more traditional uses of steel slags (e.g., landfill, fertilizer) have decreased, pointing to a need for new uses and markets. Steel slags have been used in the area of civil engineering such as the road-building aggregate or in the construction industry with caution, as free CaO dissolves in water and volume stability can thus be affected. Much research has therefore been undertaken to develop better methods of improving the properties of steel slags as well as applying them more widely and under varying conditions [*7*, *13*, *14*]. This has led to the achievement of reduced amounts of free CaO and better adaptation of these slags for uses such as road-building aggregate.

Currently, about 70% of steel slag and 95% of iron slag is used, and further research could lead to improved quality and new markets for slag. For example, improvement in hydraulic properties of slag will increase its use as an important component in cement production.

Nonferrous Slags

Slags from nonferrous pyrometallurgical manufacture, such as lead and copper, are similar in composition to ironmaking and steelmaking slags. They consist mainly of lime, silica, alumina and iron oxide, the principal constituents of rock and soil (see Table 3). While these slags also contain very small quantities of various heavy metals such as lead, chromium, copper and zinc, these metals are usually immobilized in a stable, non-hazardous iron aluminosilicate matrix within the slag [*9*]. The slag can thus be utilized as construction material aggregate, rail ballast, and road-building aggregate. Small quantities of nonferrous slags are also used to make mineral wool for use as filter media, vehicle brake linings, noise-reduction material, etc. These nonferrous slags are non-hazardous and useful co-products that do not pollute the environment.

Because the majority of nonferrous minerals contain many metals, numerous attempts have been made to use metals from their slags in order to achieve poly-utilization of the mineral resources and to decrease energy consumption. During the last decade, the slag fuming process for zinc recovery from lead slag (containing ZnO 5 ~ 25%, Table 3) has been well established [*9*]. Noranda's processing of copper from copper-rich slags generated in converting and continuous smelting, via flotation, settling, reduction, sulfidization and TBRC (Top Blown Rotary Converter) process have proved to be successful [*10*, *15*]. Other attempts to recover copper from reverberatory furnace slags by hydrometallurgical processes using nitric acid, sulfuric acid or ferric chloride have been made [*10*, *11*]. But no such process has been successful on a commercial scale.

TABLE 5. Chemical Analyses of Selected Constituents in Dusts (ppm)

Dust	Cr	Cu	Mn	Ni	Pb	Zn	Cd	Sb	Se
BOF	270–350	100–220	11,000–12,000	90–140	6,500–8,200	2,600–3,800	---	---	---
BF	30–170	13–300	2,700–31,000	20–130	90–1,00	---	---	---	---
EAF	800–2,700	520–3,400	38,000–45,000	170–500	20,00–25,00	54,000–75,000	---	---	---
Pb BF	10	5,350	---	---	82,000	---	14,000		
Cu C*	50	280,000	90	110	8,000	28,000	520	500	30
Cu RF*	45	240,000	100	35	12,000	44,000	310	750	80

*Cu C: Cu Converter, Cu RF: Cu Reverberatory Furnace; Their units are (mg/L).

It should be noted that the concentrations of nonferrous metals in the slag are essential factors when considering whether to recover the metals from slag. Only when the concentrations of metals in slag are greater than their concentrations in raw ores and the recovery cost is low, is the slag actually recycled. Thus, relatively large amounts of slags still go to landfill.

DUSTS

Dusts from metallurgical processes are collected by various dust equipment such as baghouse and electric collector. Their quantity depends mainly on gas flow, temperature as well as particle size. Because of the high metal content of metallurgical waste dusts (see Table 5), the preferred method of handling most dusts is to reprocess them [*2*]. But some dusts resulting from the smelting of various raw ores contain multiple constituents and have physical and chemical characteristics different from those of the raw ore. Some constituents are high-value elements (e.g., Cu, Ni). Some are harmful in their reprocessed form (e.g., Pb, Zn), and their disposal could pollute the environment. Treatment methods for such dusts need to be developed.

At present, intensive effort is being focused on the treatment of EAF (electric arc furnace) dust. A typical EAF operation produces a volume of dust equivalent to approximately 1 to 2 percent of the charge, depending on the raw materials used for steelmaking. This dust contains relatively large amounts of zinc and of other valuable but toxic metals such as lead, and chromium, which can leach after disposal and pollute soil and groundwater. During the last decade, many treatment methods have come into being.

The main methods of recovery of metals from EAF waste dusts are listed in Table 6 [*16*, *17*]. They can be categorized as either high-temperature or hydro-treatments. Hydro treatments produce residues which still contain toxic metals such as lead, cadmium and chromium, and can't be directly disposed of. When these co-products are recovered, they appear as a "cement" which needs additional treatment to separate out the respective metal or metal oxide. These multi-stepped approaches are rarely used commercially. High temperature thermal treatment methods, on the other hand, like older pyrometallurgical zinc processes, are generally used because the slags thus generated can be returned to the ironmaking or steelmaking process as an iron-rich material. Neither approach, however, can be applied economically to those dusts having low zinc content.

In short, remediation of EAF dusts currently involves the following possible options: zinc recovery, fertilizer, landfill (where solidification or stabilization is needed), or other products such as mineral wool, ceramic materials, and glass beads. During the last decade, the amount of EAF dust used for zinc recovery has gradually increased (see Figure 1) [*16*]. Low zinc content dusts, including zinc-containing

TABLE 6. Processes of Metals Recovery from EAF Dusts

Thermal-Recovery		Hydro-Recovery	
Process	Product	Process	Product
Waelz Kiln	Zn oxide & slag	1) Acidic Leaching Media	
HTR	Zn oxide & slag	Versatic Acid	Zinc & residue
Flame Reactor	Zn oxide & slag	Two Stage Sulfuric Acid	Zinc & residue
Inclined Rotary Reduction System	Zn metal & slag	Chloride Leach	Zinc & residue
		Chloride Sulfate	Zinc & residue
SKF Scandust	Zn metal & slag	UBC Chaparral	Zinc, Pb & residue
Sirosmelt	Zn metal & slag	Modified Zincex Process	Zinc, Pb & residue
IMS Plasma	ZN metal & slag	2) Alkaline Leaching Media	
Extended Plasma Arc Reduction	Zn metal & slag	Ammonium Chloride Leach	Zinc oxide & residue
		Ammonium Leach	Zinc oxide, Pb, Cu & residue
Pyromet-Mintek Plasma	Zn metal & slag	Chlorination	Zinc & residue
		Caustic Leach	Zinc, Pb, Cu, Cd & residue
High Temperature Metal Recovery	Zn metal, iron & slag	Cenim LNETi	Zinc & residue
Hi Plas Technology	Zn metal, iron & slag	Ammonium Carbonate	Zinc oxide & residue

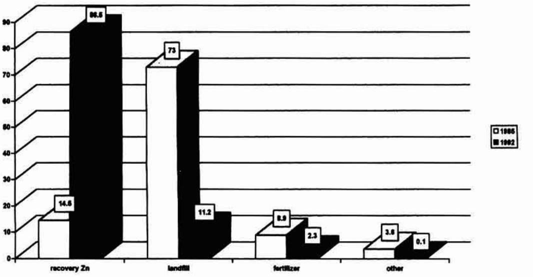

FIGURE 1 Disposal of EAF Dust in the U. S.

dusts derived from iron and steel production in basic oxygen or blast furnaces, will continue to be landfilled at least in the short term, because there are no alternative treatment methods proposed at this time which are acceptable from both economic and technological point of view. Therefore developing the new treating process of low-zinc-content dusts, which can practically be used in the technology and economic, will become good wish of researchers and firms.

Many attempts have been made to recover valuable metals from complex smelter dusts produced during nonferrous metal production. Some such processes have been adopted commercially, for example the Shenyang Smelter in China where sulfuric acid is applied in two steps to recover indium, cadmium, arsenic, bismuth and zinc from copper dust mixtures [*10*]. Swagn et al. [*18*] investigated the feasibility of applying the ausmelt process to complex copper smelter dust in order to recover copper, bismuth and gold. However, because many metal recovery processes carry relatively high costs yet do not resolve the environmental problems of dust disposal, dust treatment methods have tended to focus on the key area of arsenic and other toxic element separation and remediation [*19*]. High-temperature treatment has been widely applied in the remediation of these hazardous dusts, and such products as marketable alloys and oxides, as well as non-hazardous, disposable slags, can be obtained [*9*, *11*].

The authors think that the remediation of hazardous nonferrous dusts will focus on the development of a multi-process, which allows for simultaneous recovery of valuable metals and treatment of non-hazardous slag.

SLUDGES

There are three types of sludges resulting from both pyrometallurgical and hydrometallurgical processes: 1) Discarding matters from hydrometallurgical process of metal extractions (e.g., red mud, zinc residues); 2) Residues from treatment processes of metallurgical wastewater; 3) Precipitate matters from gas scrubber water in collecting dust system. These sludges have a high and complex metal content. Since the composition of most sludges is similar to that of the raw materials from which they are generated, they can be fed back into the production process after dewatering. Some sludges, such as those generated by electrorefining or electrowinning of heavy metals, have been successfully used as a source for the extraction of rare and precious elements such as platinum, gold and silver. These treatment methods are well understood and will not be dealt with here. Three sludges generated by primary metals industries and having a major environmental impact (see Table 7) [*1*] are addressed in the paper; namely, sludges from harmful wastewater treatments in ironmaking and steelmaking, red mud generated during the alumina production, and zinc residues generated by the removal of impurities during of hydro-extraction of zinc.

Iron and Steel Sludges

Of the many sludges generated in ironmaking and steelmaking, the treatment of two types is particularly difficult. One is the sludge produced by cokemaking plants which contains ammonia and other organic compounds (e.g., benzene, toluene and xylene). The other is the sludges generated by pickling, galvanizing and rolling mills which contain toxic metals (e.g., chromium, zinc, and lead), organic compounds and oil. Because both types of sludges contain very large amounts of water and dewatering consumes great amounts of energy before treatment of the polluting substances can even begin, nearly all factories make reducing waste generation as their first approach. For example, they separate the sludge from the wastewater in order to feed it back into the process. It allows to achieve non-hazardous waste output and reduces the quantity of waste. Traditional approaches to the treatment of wastewater, usually mechanical or chemical, which involve higher costs, more time and additional space, are gradually being replaced by newer approaches such as biological treatment [*20*, *21*], membrane filtration [*22*, *23*, *24*], flotation [*22*, *25*], and microwave treatment [*26*]. The adoption of these newer processes has resulted in more effective treatment of wastewater, reduced costs and a sharp reduction in sludge quantity. Iron and steel sludges can now either be fed back into the process or their hazardous constituents treated, if necessary, prior to disposal.

Yet another option is to combine these hazardous sludges with other ironmaking and steelmaking wastes such as baghouse dust, slag, concentrated acid waste, salt sludge, etc. in ways that produce non-hazardous residues by merely solidifying them [*27*, *28*]. This type of treatment process is shown schematically in Figure 2. It is an efficient

TABLE 7. Major Wastes Needing Resolvement in Primary Metal Industries

Waste Type	Fe*	Al	Cu	Zn	Mg	Ti
Gas	CO_2	HF, CO_2, Volatile	SO_2	SO_2, Cd	CHCs, Dioxin	CO_2, Volatile chlorides
Sludge	Wastewater	Red Mud	----	Iron oxide, Cd	----	$FeCl_3$
Solid	ZnO dusts	Spert pot, Tar pitch	Metal fumes	---	----	---

*Fe: including both iron and steel.

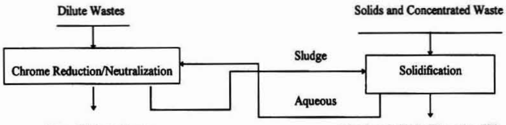

FIGURE 2 Schematic Process of Sludge Treatment

way of using wastes to treat wastes. In this process, the dilute waste containing harmful substances from pickling mill (e.g., Cr, Cd) and a spent pickle acid combine with lime slurry in neutralization process. As a result, a dilute metal hydroxide sludge is continuously generated. It subsequently goes to the solidification process for further processing with solids (e.g., baghouse dust, crushed slag, and lime) and concentrated liquids (e.g. spent H_2SO_4/HCl, fresh acid). Residues after solidification can be directly landfilled, and water is returned to the neutralization process. Thus, this process consumes wastes generated and converts hazardous wastewater, dust and slag into a non-hazardous product which can be used for landfilling without any pre-treatment.

Red Mud

Red mud is the waste sludge generated by the Bayer process (the basic digestion of bauxite) of alumina production. For every tone of alumina, about one tone of red mud is generated. For example, production of one tone of aluminum will generate about 2.5 tones of red mud. For environmetally safe disposal, red mud must be confined in large tanks.

The key properties of red muds are listed in Table 8 [*5*, *29*] and Table 9 [*29*]. As shown in these tables the major components of red muds are Fe_2O_3, Al_2O_3, SiO_2 and Na_2O. It also contains trace amounts of metallic elements such as vanadium, galena, chromium, magnesium, and zirconium. Its major mineral constituents include hematite, goethite, anatase, rutile, quartz and sodalite. Clearly, red muds are a potential source of many valuable metals.

During the last few decades, much research has been undertaken to develop techniques for the extraction of rare and precious metals from red muds [*10*, *29*]. Investigations into recovery of titania, for example, have yielded many approaches, such as gravity concentration, chlorination, sulfuric acid digestion, hydrochloric acid digestion, and SO_2 treatment [*10*, *29*].

TABLE 8. Physical and Chemical Properties of Red Mud

1) Major Constituents		Minor Constituents	
Properties	Range (%)	Properties	Range (%)
LOI* (1000°C)	10 ~ 12	P_2O_5	0.20 ~ 0.40
Fe_2O_3	30 ~ 35	V_2O_5	0.20 ~ 0.40
Al_2O_3	16 ~ 20	MnO_2	0.05 ~ 0.10
TiO_2	15 ~ 18	Cr_2O_3	0.05 ~ 0.10
SiO_2	8 ~ 10	SO_3	0.05 ~ 0.10
Na_2O	2 ~ 40	MgO	0.05 ~ 0.10
CaO	6 ~ 12	ZnO	0.01 ~ 0.05
		Ga_2O_3	Trace ~ 0.01

2) Physical Properties:
Color Rust red
Density (g/mL) 2.6 ~ 3.2
Specific surface area (m^2/g) 20 ~ 40
pH value (10g/100mL of water) > 11
Particle size Sands (> 230 μm) 10%; Fines (clay-like) 90%

3) Liquor Composition:
Titralde soda (decrease with washing) 8 ~ 12 (g/L)
Soluble alumina 2 ~ 4 (g/L)

4) Mineralogical Constituents
Hematite, Goethite, Rutile, Anatase, Gibbsite, Sodalite, Quartz etc.

*LOI: Loss on ignition

TABLE 9. Properties of Main Natural Minerals Present in Red Mud [29]

Parameters	Hematite	Goethite	Anatase	Rutile
Chemical formulae	Fe_2O_3	FeO OH	TiO_2	TiO_2
Crystal system	Trigonal	Orthorhombic	Tetragonal	Tetragonal
Sp. gravity	5.2 ~ 5.3	4.1 ~ 4.3	3.8 ~ 3.9	4.2 ~ 5.5
Hardness (Mohs)	5.0 ~ 6.0	5.0 ~ 5.5	5.5 ~ 6.0	6.0 ~ 6.5
Color	Dull red to Black	Yellow to Brown	Yellow to Brown	Reddish brown to black
Acid solubility in HCl	Soluble	Soluble	Insoluble	Insoluble

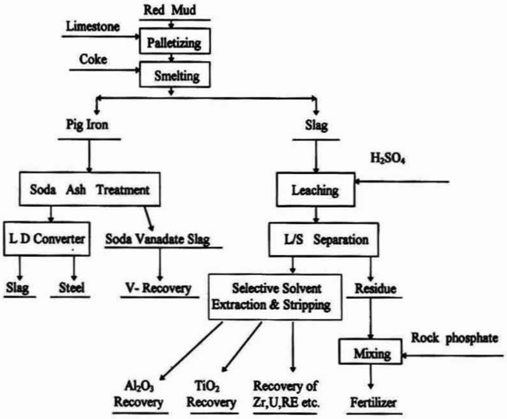

FIGURE 3 Conceptual Flowsheet for Complete Utilization of Red Mud

For the recovery of trace elements (e.g., vanadium, galena, zirconium, uranium) and rare earth metals from red mud, Shamsuddin [*10*] recommends a scheme of reduction smelting and sulfuric acid digestion. This process is similar to the multi-utilization process (Figure 3) recommended by Prassad [*10*]. During smelting, valuable elements (e.g. Al, Ti, Zr, P, U) are concentrated in slag while vanadium goes to pig iron. The element present in the smelting slag can be further separated by regulating the pH of the solution in the leaching process [*12*]. The residue left by leaching of the slag is usually used as fertilizer when mixed with raw phosphate. Finally, vanadium can be extracted from the vanadium-rich slag obtained from pig iron smelting.

A number of researchers [e.g., 5, 10, 29, 30] have found ways of utilizing solid wastes obtained from red muds. For example, Na_2O which is recovered by the processes of mixing with soda and washing can be reused in alumina production. However, none of these methods has been commercially developed. One major obstacle is the relatively high cost involved. The other is the particular characteristics of red muds. Because they contain very large amounts of crystalline water and are very fine (see Table 8, LOI = 10 ~ 12%), their dewatering by any flocculation, precipitation, centrifuging or filtration procedures is both difficult and very expensive. Even for purposes of iron and steel production or the manufacture of low-density bricks, red mud treatment nevertheless requires costly dewatering. Once again, commercial feasibility demands that the cost of recovering elements from wastes, including the cost of waste treatment, must be less than the value of those elements within the raw ore. Thus, from a technological and economic viewpoint, prospects for single-element recovery or single-product utilization of red muds are very uncertain, yet the need remains for methods to curtail or eliminate the proliferation of red mud tanks. In recent years, research into red mud utilization has been redirected to development of poly-element or poly-utilization treatments (e.g., process shown in Figure 3) to decrease the cost of red mud remediation. In this process, red mud is palletized with limestone and smelted. Pig iron is subsequently produced which consists of vanadium and multi-metal-containing slag. Vanadium can be recovered by soda-vanadate treatment while other metals (e.g., Al, Ti, Zr, U) could be recovered by leaching and separating processes.

Zinc Residues

More than 80 percent of the worldwide primary zinc is produced via a combined roast-leach-purification-electrowinning process. It is based on roasting the concentrate containing zinc sulfide mineral to produce sulfuric acid. A part of the acid can be used to leach the roasting product and to obtain zinc. Problems of hazardous emissions (such as SO_x and heavy metals) are later addressed in the traditional smelting process.

During the 1970s, and early 1980s, this process was considered a modern and environmentally sound method of producing a primary metal. But it introduced a new environmental problem, the hazardous residues generated during removal of a large amount of iron from the zinc-leaching liquor. In normal practice, for every tone of zinc produced, about 0.4 tone of waste residue results. This waste residue has been listed as a hazardous substance for nearly a decade, and is currently landfilled in various types of storage containers. The disposal and management of these residues has become the overriding problem of electrolytic zinc production.

Depending on the types of purifying materials used to remove iron during production, three main kinds of residues, described in Table 10, can be generated: jarosite, goethite or hematite [*31, 32, 33*].

Of the three residues, hematite has the highest iron and lowest zinc content and can be used in other industries such as cement, ceramic, etc. But despite these properties, hematite is not acceptable for iron and steel production as an ironmaking material, because even small amounts of zinc in the blast furnace charge cause refractory problems and contribute to the tonnage of flue dust produced. Most

TABLE 10. Comparison of Zinc Residues

Process Formula		Metal Components (%)					Relative Costs	Capital Operating	Pond Volume Required m^3/year	Possible Uses
		Zn	Cu	Cd	Pb	Fe				
Geothite	$Fe_2O_3 \cdot H_2O$	2.3	0.5	0.05	2.2	41	1.70	0.94	51,700	Not known
Jarosite	$2(M)Fe_3(SO_2)_4(OH)_6$	3.0	0.2	0.02	1.5	30	1.00 ~ 1.51	1.00 ~ 1.16	76,800 ~ 79,980	Not known
Hematite	Fe_2O_3	1.3	---	0.01	---	60	1.58	2.01	69,400	Cement, Ceramic, Ironmaking

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$M = K^{1+}, Na^{1+}, NH_4^{1+}, Ag^{1+}, H_3O^{1+}, Pb^{2+}$ etc.

blast furnace operations require that zinc content of less than 0.01% in raw materials, considerably less than the zinc content of hematite. For the same reason, such use of either goethite or jarosite is precluded, even though a goethite process would otherwise generate a disposal pond volume about 30% and 25% smaller than with jarosite use and hematite use respectively. However, the capital costs for conversion to goethite are relatively high [*32*].

In recent decades much research has addressed both extraction of valuable metals from these three types of waste residue and reduction of the residue volume. For example, in the jarosite process, several methods are successful in recovering lead, silver, gold, copper and cadmium [*29*]. In Japan, one such combination process is used to extract zinc, lead, cadmium, gallium, indium, gold, silver and copper from residues [*10*]. A process flowsheet of this process for the complete utilization of zinc residues to recover copper, zinc, cadmium, gold, indium and silver is shown in Figure 4. Addressing the reuse and disposal of zinc residues, Dutrizac [*32*] and Piskunovo et al. [*34*] respectively investigated the feasibility of converting jarosite, via thermal deposition, into compact hematite and its subsequent use to produce iron oxide pigment, cement, and pig iron. While this approach has the merit of reducing the volume of the jarosite residue, it is too expensive. Additionally, because compact hematite still contains 0.2 ~ 0.3% zinc it is unsuitable as an ironmaking material, and due to its relatively high level of impurities, is not ideal for making pigment either. Its market is therefore very limited.

Practical processes enabling large-scale use of zinc waste residues have still not succeeded, although a few processes have been developed for successfully extracting selected nonferrous metals from these residues (e.g., Pb, Zn, Cu, Cd, Au, Ag, In). Sizable capital investment in pyrometallurgical processes will be required for the industry to successfully treat zinc residues and achieve compliance with environmental laws [*9*]. The authors intend to research and develop a thermal process applicable to direct ironmaking that would achieve significant utilization of zinc residues. A scheme of the investigated process is depicted in Figure 5. Pellets would be formed by combining the residues with coke, lime, and quartz. In the prereducing procedure, jarosite would decompose and zinc and lead would be volatilized and reduced. After the remaining pellets underwent reducing smelting in reactors such as electric or plasma furnaces, iron and non-hazardous slag would be obtained. SO_2 generated in the prereducing process could be used in producing sulfuric acid, and ZnO dust could be returned to the zinc leaching process. Low-zinc-content dust from the reductive smelting would be used together with EAF dust for zinc recovery or returned to the process as a mixing material. Thus, this process can simultaneously recover Fe, Zn, and S in the residues and generate the non-hazardous slag. The slag waste could be reused or disposed by landfill. Since the slag properties are not hazardous therefore, the possible environmental impact should be significantly decreased. It is expected however, that zinc and lead volatilization and reduction during prereducing will be difficult to control. Solving the problem of zinc residues would in fact be helpful not only for the electrolytic zinc industry but also for development of a similar process to be applied to the hydrometallurgical treatment of EAF dusts.

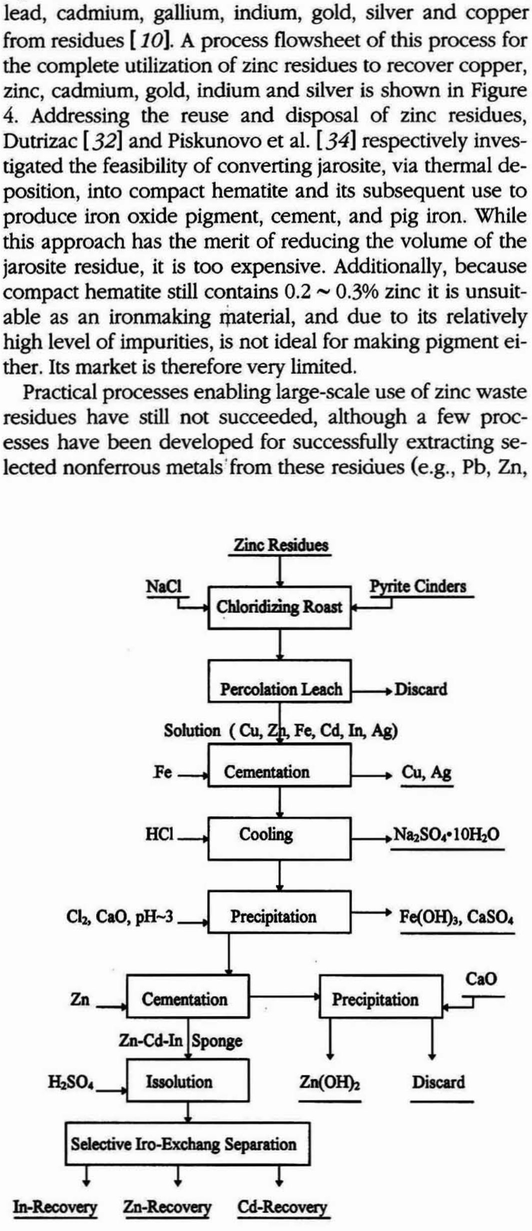

FIGURE 4 Flowsheet of the Utilization of Zinc Residues

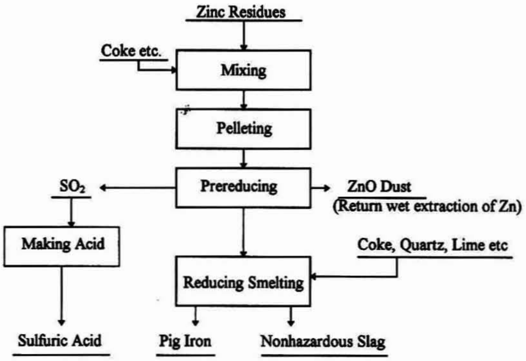

FIGURE 5 Proposed Process of the Complete Utilization of Zn Residue

CONCLUDING REMARKS

The primary metals industry has an important role to play in improving the environment. Solid waste remediation technologies, such as stabilization or solidification, incineration, and hydrometallurgical metal recovery, have been applied in the industry and new technologies such as plasma and vitrification processing of solid wastes are under development. On the whole, however, solid residue remeidation remains relatively uncommon, and currently applied technologies are unable to solve the complex problems of metallurgical solid wastes (such as dusts from ironmaking, steelmaking and heavy metal smelters, red muds, and zinc residues) described in this paper. Mean-while, new legislation has classified formerly unregulated materials such as smelter of nonferrous metals and steelmaking furnace dusts, as well as zinc residues, as hazardous wastes requiring treatment before disposal. The ever-increasing quantities of these wastes underlines the need for effective waste remediation methods.

High-temperature treatment in which metallurgical furnaces are used as remediation reactors holds great potential as an alternative disposal method. Such thermal treatment could reduce the waste to a fraction of its original volume and mass, and remediation is immediate rather than requiring long-term residence in biological treatment ponds or other forms of land disposal. Furthermore, heat recovery techniques could reduce or offset the cost of operation by the use or sale of the energy generated.

The trend today is toward increasing use of thermal remediation for a wider profile of wastes. However, information on the behavior of pollutants in industrial-sized reactors is scarce due to the complexity of the phenomena involved and inaccessibility of such systems to detailed experimental studies that would permit fundamental interpretation. A study of the simultaneous destruction of toxins and extraction of multiple metals in lab-scale or pilot-scale thermal remediation systems would be of practical significance. It is clear that essentially new engineering approaches are needed to develop solid waste remediation processes that maximize the extraction of valuable and resuable resources, reduce the toxicity and volume of waste to the greatest degree possible, and thus satisfy environmental regulations.

ACKNOWLEGMENTS

We would like to thank Ms. Linda Meissenheimer for invaluable technical support.

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Remediating Pesticide Contaminated Soils Using Solvent Extraction

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Bench-scale solvent extraction studies were performed on soil samples obtained from a Superfund site contaminated with high levels of p,p′-DDT, p,p′-DDD, p,p′-DDE and toxaphene. The effectiveness of the solvent extraction process was assessed using methanol and 2-propanol as solvents over a wide range of operating conditions. It was demonstrated that a six-stage methanol extraction using a solvent-to-soil ratio of 1.6 can decrease pesticide levels in the soil by more than 99% and reduce the volume of material requiring further treatment by 25 times or more. The high solubility of the pesticides in methanol resulted in rapid extraction rates, with the system reaching quasi-equilibrium state in 30 minutes. The extraction efficiency was influenced by the number of extraction stages, the solvent-to-soil ratio, and the soil moisture content.

Various methods were investigated to regenerate and recycle the solvent. Evaporation and solvent stripping are low cost and reliable methods for removing high pesticide concentrations from the solvent. For low concentrations, GAC adsorption may be used. Precipitating and filtering pesticides by adding water to the methanol/pesticide solution was not successful when tested with soil extracts.

INTRODUCTION

The number of Superfund sites that have pesticide contaminated soils has been increasing. At present, there are more than 48 sites on the CERCLA National Priorities List (NPL) and more than 44 non-NPL sites that are contaminated with organochlorine pesticides [*1*]. Many of these sites have been used for formulating, blending, packing, and distributing agricultural pesticides. Soil and groundwater contamination at these sites resulted from leaks, spills, and residue disposal from manufacturing processes. Most organochlorine compounds have been used as insecticides or fungicides. Although most of these compounds are banned in the U.S., they still persist in the environment. The commonly found pesticides at Superfund sites are halogenated organics that include dichlorodiphenyltrichlorethane (p,p′-DDT), toxaphene, hexachlorocyclohexane (HCH), endrin, and aldrin [*2, 3*]. These pesticides have very low water solubility, bioaccumulate in the environment, and have acute mammalian toxicity. Some of them are carcinogenic and some may be estrogen mimics [*4*].

In the past, remediation options for pesticide contaminated soils were limited to costly high temperature incineration or disposal in off-site hazardous waste landfills. Recently, a variety of other technologies, including solvent extraction, thermal desorption, and alkaline hydrolysis have been shown to be effective alternatives along with others listed in Table 1 [*1*].

Previous bench- and pilot-scale treatability studies have shown that solvent extraction is an effective method for remediating soils contaminated with organic wastes [*5*]. Developing a solvent extraction process requires understanding of the influence of soil characteristics, solvent properties, and process variables on the rate and effectiveness of extraction.

This paper presents results of bench-scale solvent extraction studies performed on pesticide contaminated soils obtained from the Aberdeen Pesticide Dump Site in North Carolina. The objectives of this study were to: (1) select appropriate solvent or solvent mixtures; (2) identify factors that affect the rate and efficiency of extraction, such as the method of contacting, solvent-to-soil ratio, pre-treatment procedures, soil characteristics, and the number of contacting stages; and (3) investigate cost-effective methods for solvent recycling, recovery of solvent from the soil after processing, and volume reduction of concentrated contaminants. Long term objectives are to (1) optimize the design and operation of the process to achieve remediation goals; (2) determine the process parameters required for pilot-plant design; and (3) investigate options for post-treatment of the soil and the extract.

TABLE 1. Soil Remediation Technologies at National Priorities List Pesticide Sites (*1*)

Remedial Technologies	Number of Sites
Incineration	8
Multi-layer capping	6
Off-site disposal	8
Thermal desorption	4
Soil washing	2
Dechlorination	2
Anaerobic bioremediation	1
Vitrification	1
Solvent extraction	6
Not available	5

Solvent Extraction Overview

Solvent extraction is a method of removing contaminants from a solid phase by contacting the solids with a non-aqueous fluid that dissolves and mobilizes the contaminants. The fluid is separated from the solids and reclaimed. This results in reducing the volume of the contaminated phase that requires further treatment or disposal. The process involves solubilization of contaminants from the particle pore space, diffusion of contaminants from the solid, and washing the extract from the surface of the solids. The fluids used are usually organic solvent, liquefied gases, or supercritical fluids that have a high affinity for the contaminants. Solvent extraction has been demonstrated to be an effective method for reducing contaminants below the action levels for sediments and soils contaminated with PCBs, oil refinery wastes, and pesticides [*6*, *7*].

A flow diagram for a typical solvent extraction system is shown in Figure 1. The process consists of soil extraction and solvent recovery. At present, solvent extraction has been chosen as the selected remedy at eight Superfund sites. Several extraction systems have been proposed and tested under the auspices of EPA's Superfund Innovative Technology Evaluation program. These systems were investigated for degree of contaminant reduction achieved, treatment cost, and emission problems. Most of these systems have been tested on PCB contaminated soils and sludges, and have been shown to reduce concentrations of PCB from the contaminated sediment by more than 99 percent [*8*]. Each extraction system has a unique contacting method, solvent type, and requirement for pre- or post treatment [*9*, *10*]. Some of the factors that can affect performance of solvent extraction processes are waste characteristics, solvent properties, and process variables [*11*]. Selection of the best extraction solvent for a particular contaminant is not obvious and extraction efficiencies vary for different types of soils, levels of contaminant, and site-specific parameters. Important solvent properties include dissolving power, cost, volatility, flammability, surface tension, and heat of vaporization. The solvent of choice should have a strong affinity, or dissolving power, for pesticides, allow fast extraction, and can easily be separated from the pesticides. For sediments and soils with a high moisture content (> 20%), water around the soil particles creates a barrier for extraction. In such cases, either dewatering is required as a pretreatment step, or the solvent of choice must be hydrophilic. If the solvent forms an azeotropic mixture with water, then the azeotrope should have a water content of less than 20% to minimize dilution of the solvent by the soil moisture. To get an easy soil-solvent separation, the solvent should allow a fast settling rate for solids. Additionally, the solvent used must not be an EPA listed hazardous waste.

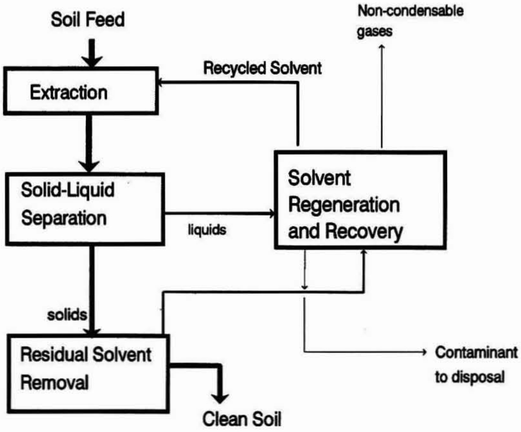

FIGURE 1 Flow diagram for a typical solvent extraction system.

Many solvent extraction systems are in the final phase of pilot-scale development and few full scale units are in use. However, there are still many fundamental questions and performance problems that require investigation. This study intended to provide a better understanding of the solvent extraction process and to obtain design parameters for a pilot-plant system.

Materials and Methods

Soil samples for this study were obtained from the Aberdeen Pesticide Dump Site located in North Carolina. The site has a well drained sandy surface soil and sandy loam subsurface soil. Samples were collected from locations that were shown to contain organochlorine pesticides based on previous investigations made by U.S. EPA, Region 4. The collected soil was passed through a 2 mm screen, debris was removed, and the screened soils were stored in sealed containers. The soil moisture content, measured using a gravimetric method, was about 12% and the particle size analysis [*12*] has shown that the soil was coarse. Fines (75 μm or less) constitute less than 10% of the soil mass and the average particle size was 300 μm.

Experiments were done to determine the effects of treatment time, soil-to-solvent ratio, and the number of extraction stages. Solvent extractions were performed using a two-liter batch extractor equipped with a stirrer and two ports for liquid and solid sampling (Fisher Scientific K614000-2000). A propeller mixer with a speed of 1,200 rpm was used to keep the slurry in suspension. For each run 100 grams of soil (dry weight) and 164 to 420 ml of solvent were placed in the extractor. The extractor was initially operated at room temperature (22°C) for 120 minutes. However, the extraction time was reduced to 30 minutes after results from initial experiments indicated that a lengthy extraction time was unwarranted.

At the end of each run the soil was allowed to settle before the supernatant solvent was decanted. Samples of the solution (10 ml) and the soil (~ 5 g) were then withdrawn. The solvent samples were filtered immediately after collection to avoid further extraction in the sample vial. The soil samples were kept in a fume hood at room temperature (22°C) and the residual methanol was allowed to vaporize. The soil samples were then extracted with acetone for two hours in a 50°C sonicator bath followed by centrifugal separation of the soil from the solvent (SW-846, Method 8080) [*13*]. The extract was then diluted and analyzed using an HP 5890 GC equipped with an electron capture detector (^{63}Ni) and a 30 m × 0.32 mm fused silica capillary column (J&W Scientific, Folson, CA) with DB5MS stationary phase having a film thickness of 0.25 μm.

Results of Extraction Studies

The organochlorine pesticides found at the Aberdeen Pesticide Dump Site include toxaphene, *1,1,1-trichloro-*

TABLE 2. Waste Profile and Concentration of Critical Contaminants in Soil Sample Obtained from the Aberdeen Pesticide Dump Site, North Carolina

Parameter	Avg. Conc. in Sample Soil (mg/kg)
p,p′-DDT	5,085
p,p′-DDE	115
p,p′-DDD	2047
Chlordane	45
Aldrin	5
Dieldrin	5
Endrin	11
Toxaphene	1,300
Heptachlor	160
Total Pesticide	8,773
Dioxins* (ppb)	2.15
TOC	15,900
Mean particle Size	300 μm
Percentage of fines	< 10%

TOC—Total Organic Carbon
*Total Equivalent Quantity

2,2,-bis(p-chlorophenyl)ethane (p,p′-DDT), *1,1,-dichloro-2,2-bis(p-chlorophenyl)ethane* (p,p′-DDD), *1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene* (p,p′-DDE), endrin, aldrin, chlordane, dieldrin, and heptachlor. The contaminant that exhibited the highest average soil concentration, 5085 mg/kg, was DDT. The total average pesticide concentration was 8773 mg/kg. The pesticide concentrations and characteristics of the soil are summarized in Table 2. Since DDT, DDD, and DDE were the three major contaminants, they were used as indicator compounds to measure the extraction effectiveness (Table 3). The contaminant concentrations of the treated media must be below the site specific cleanup levels (Table 4).

Effect of Extraction Time

Extraction time, which is the contact time between the solvent and the contaminated soil, affects the treatment performance. Sufficient time must be provided to effectively extract the contaminant from the waste. The time necessary to extract a given contaminant is dependent on the solubility of the contaminants and the desorption of the contaminants from the organic matter in the soil.

All of the pesticides except toxaphene have a solubility above 15 g/L of methanol. For this study the extraction rate was rapid. Residence times of more than 30 minutes only marginally improved the extraction (Figure 2). Therefore, extraction times were kept constant at 30 minutes of the remainder of the study.

TABLE 3. Major Pesticides in Untreated Soil (Average of 16 Samples) Aberdeen Pesticides Dump Site, North Carolina

Statistic	DDE	DDD	DDT
Mean conc. (mg/kg)	115.3	2,047.1	5,085.8
Standard deviation (mg/kg)	33.8	319.4	598.5
Coefficient of variance (%)	29.3	15.6	11.7

CV = 100* (mean/stand dev.)

TABLE 4. Treatment Standards for Contaminated Soils

Waste	Cleanup Level (mg/kg)
p,p′-DDT	11
p,p′-DDE	10
Aldrin	20
Endrin	20
Toxaphene	6
α-BHC	1
β-BHC	2
γ-BHC	3
Heptachlor	0.78

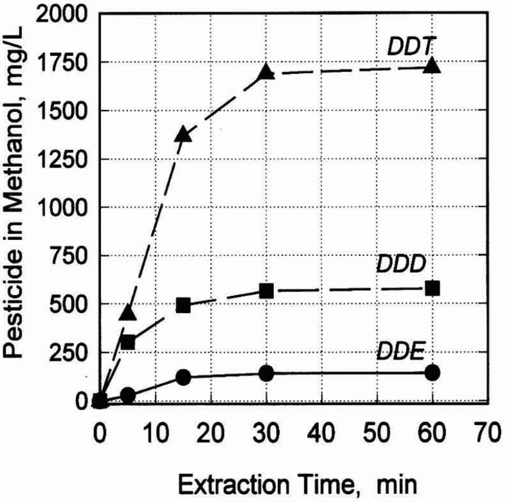

FIGURE 2 Effect of time on extraction of p,p′-DDT, p,p′-DDD, and p,p′-DDE using a L/S ratio of 2 from soil having 12% moisture content.

Effect of Number of Extraction Stages

Multiple extractions were necessary to achieve the low cleanup goals. Multi-stage extractions were conducted using 30 minute extraction runs for each stage followed by settling and decanting the solvent. The soil had a 12% moisture content and the solvent-to-soil (L/S) ratio used was 1.3 (by weight). Results of multi-stage extraction experiments using interconnected mixer-separator stages showed residual DDT, DDD, and DDE in the soil decreased logarithmically as the number of stages increased (Figure 3). The first and the second extraction stages removed 60% and 85% of the contaminants, respectively. However, stage efficiencies decreased with the increase of extraction stages, requiring up to six stages to obtain cleanup levels. Initially the concentration gradient between the soil contaminants and the clean solvent is high. After completion of the first cycle, the contaminant concentra-

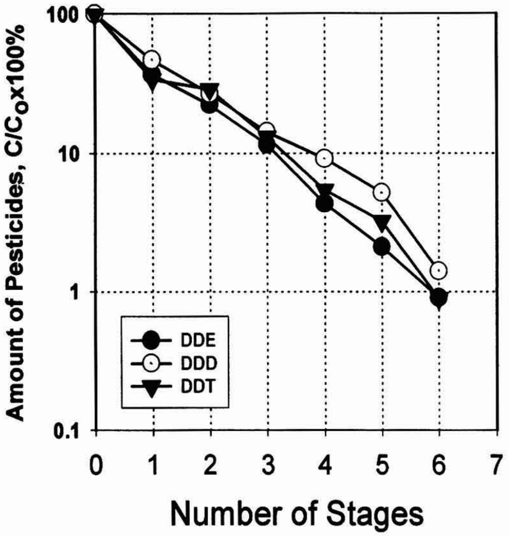

FIGURE 3 Effect of the number of extraction stages on methanol extraction of pesticides (C_o = initial concentration of DDE in the soil).

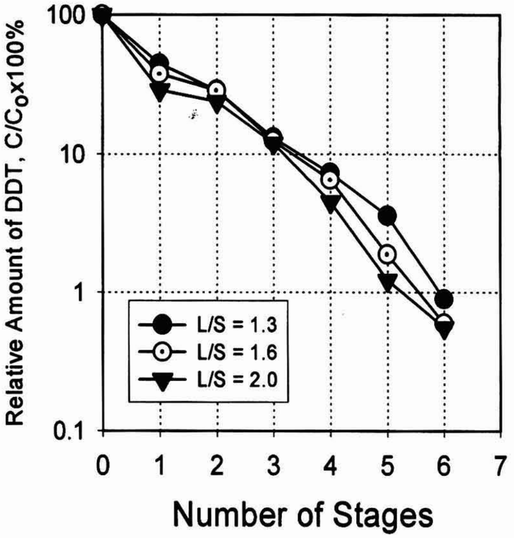

FIGURE 4 Effects of methanol-to-soil ratio on a multistage extraction of DDT.

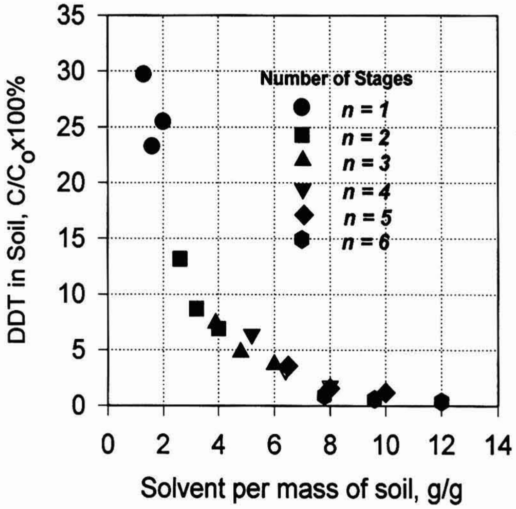

FIGURE 5 Effects of solvent amounts on DDT extraction for varying L/S ratios (1.3 to 4) the number of stages (n = 1 to 6).

tions associated with the soil are reduced to a level below the initial contaminant concentrations, thus reducing the concentration gradient between the remaining contaminants and the solvent during subsequent extraction cycles. Therefore, removal efficiencies are lower with each additional extraction stage.

Effect of Solvent-to-Soil Ratio

Solvent-to-soil (L/S) mass ratio is an important process variable that affects the performance of the extraction process. Higher L/S ratios increased removal of the pesticides from the soil; they also generated a larger volume of solvent that needed to be regenerated and recycled. Residual contaminants in the soil from multi-stage extractions using a L/S ratio of 1.3, 1.6, and 2 are shown in Figure 4. Although higher L/S ratios gave lower residual contaminants in the soil, the effect was minimal for the range of L/S ratios used. The two important process variables which determine the operation cost and the level of residual contaminants in the soil are the number of extraction stages and L/S ratio for each stage. These two variables are coupled and determine how much solvent must be used for extraction and recovered for recycling to achieve the required level of remediation. The residual DDT concentrations continuously decreased with an increase in solvent amounts for different L/S ratios and number of stages (Figure 5).

Effect of Soil Moisture

Moisture associated with soil particles can interfere with the extraction process by creating barriers between the contaminants and the solvent. High moisture contents can dilute a hydrophilic solvent and reduce the solvent strength. Soils having moisture contents of 0%, 12% and 25% were extracted with methanol for 30 minutes using a solvent-to-soil mass ratio of 1.6. Single-stage extractions showed that as the soil moisture content increased, from 0% to 25%, the extraction efficiency decreased from 89% to 66% (Figure 6). This effect of moisture was lower for higher solvent-to-soil ratios, which suggests that dilution of the hydrophilic solvent was responsible for lower extraction efficiencies. When multiple extraction stages were used the effect of soil moisture on the extraction efficiency became insignificant. This is expected since hydrophilic solvents effectively dehydrate the solids during the first extraction cycle.

Influence of Solvent Type

The primary criteria for solvent selection was the dissolving power. Other factors, such as cost, volatility, flamma-

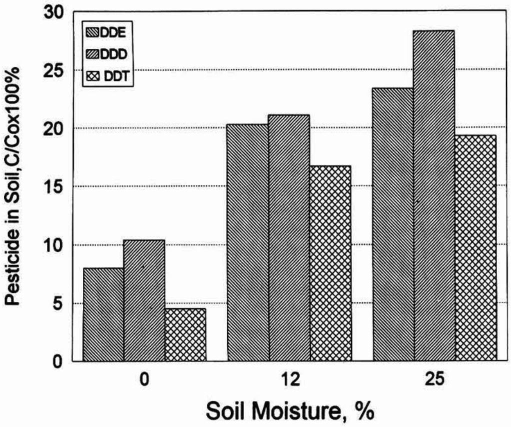

FIGURE 6 Effect of soil moisture on single-stage extraction of pesticides using a L/S ratio of 1.6.

bility, surface tension, and heat of vaporization were also considered. The dissolving power of solvents was estimated by comparing the solubility parameters, δ, of the solvents and the contaminants. The solubility parameter is the total molar cohesive energy which holds the molecules together. If the solubility parameters of two liquids are identical or differ by not more than 1 $(cal/cm^3)^{1/2}$ then they are miscible. The solubility parameters of the primary pesticides (Table 5) were calculated using the group contribution method, according to Fedros [*15*], and the solubility parameter of the solvents were obtained from standard tables [*16*]. Isopropyl alcohol (2-propanol) was selected since its solubility parameter, 11.5 $(cal/cm^3)^{1/2}$, is close to that of the primary pesticides. Another important factor was water miscibility. Most of the non-polar, halogenated organic pesticides have very low water solubility. When hydrophobic solvents are used the water film around the soil particles becomes a barrier for contaminant transfer, which creates a rate limiting step. With hydrophilic solvents the rate of transfer of the solvent from the bulk solution to the soil surface is rapid. Methanol was selected as a second solvent because it is inexpensive, noncorrosive, nonexplosive, nonreactive, is easily removed and recovered, and is highly soluble for pesticides. Methanol dehydrates the soil which assists in breaking up agglomerated soils into discrete particles.

TABLE 5. Physical and Chemical Characteristics of Pesticides (*15, 16*).

Parameter	Formula	Molecular Weight	Solubility Parameter δ $(cal/cm^3)^{1/2}$
p,p′-DDD	$C_{14}H_{10}Cl_4$	320.0	11.69
p,p′-DDE	$C_{14}H_6Cl_4$	316.0	11.74
p,p′-DDT	$C_{14}H_9Cl_5$	354.5	11.70
BHC	C_6Cl_6	285	11.88
2-Propanol	C_3H_7OH	60	11.5
Methanol	CH_3OH	32	14.5

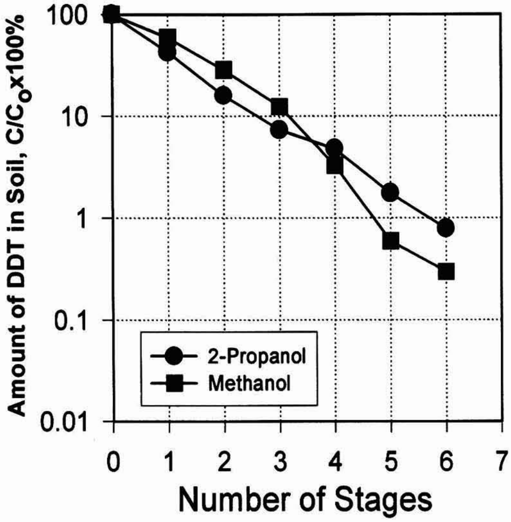

FIGURE 7 Multistage extraction of DDT using methanol or 2-propanol and a L/S ratio of 1.6 from soil with 12% moisture.

Each of the two hydrophilic solvents, methanol and 2-propanol, was effective in extracting pesticide from contaminated soils. Methanol and 2-propanol have a boiling point of 64.7 and 82.5°C and a viscosity of 0.55 and 2 cP, respectively. 2-propanol is less toxic than methanol and forms an azeotropic mixture with water at 88%; therefore, to completely separate a water/propanol mixture using distillation is not possible. 2-propanol is also four times more expensive than methanol. Although most pesticides have higher solubilities in methanol than in 2-propanol, a six-stage extraction using a solvent-to-soil ratio of 1.6 gave comparable extraction efficiencies for both solvents (Figure 7).

Other Factors

For the current study, temperature, pH, and the degree of mixing were kept constant. Temperature and pH can affect equilibrium conditions and consequently the effectiveness of the extraction. A propeller with a speed of 1,200 rpm was assumed to be sufficient to provide high mass transfer of the contaminants from the soil. Achieving sufficient mixing depends on sound extractor design and optimum operating conditions. The best mixing system may have to be determined using pilot-scale equipment. Soil characteristics, such as soil particle size and the fraction of humic material, can affect mass transfer rate and the adsorption of the contaminants. The molecule p,p′-DDT has an acidic hydrogen present on the carbon sited between the rings. Because of this slight acidity p,p′-DDT tends to bind to soil organic matter. As a result, extraction of DDT from soils with high organic contents may be slower [*17, 18, 19*].

Soil-Solvent Separation Methods

At the end of each extraction run, soil/solvent separation was achieved using gravity settling. The settling period that follows the extraction depends on the soil particle size and density and the solvent density and viscosity. Separation of the coarse soil fraction (> 75μ m) from methanol was fast and complete. Phase separation was observed within the first minute. This is due to the large density difference between the soil and methanol and the low viscosity of methanol. The more effective this separation, the less extract left in the sludge at the end of the separation and thus, the higher the extraction efficiency. Therefore, fewer extraction stages are necessary to achieve cleanup goals.

Solvent-Pesticide Separation Methods

After the solvent has been separated from the soil, the solvent undergoes further processing which concentrates the pesticides and permits solvent recycling. Proper recovery and recycling of the solvent can significantly affect the cost of the overall treatment process. Experiments have shown that when a six-stage extraction was used, the solvent used after the third stage may be recycled without being regenerated, because the contaminant levels in the solvent are low (less than 10 ppm). Spent solvent following the third extraction cycle was used for the first two extraction cycles for the next charge of soil. Results showed that high extraction efficiencies (more than 99%) were achieved while operating in this mode.

To separate the pesticide/solvent mixtures and recycle the solvent, different methods were investigated. These methods were precipitation of pesticides by adding water to the extract, evaporation of the methanol, adsorption using granular activated carbon, and liquid/liquid extraction using hexane.

Precipitation

A study conducted by Roebeck et al. [*20*] showed that DDT can easily be removed from aqueous solutions by settling and coagulation followed by filtration. Cohen et al. [*21*] showed that alum coagulation is effective in removing pesticides, like toxaphene, from aqueous solutions. In the current study, it was experimentally demonstrated that when water was added to the methanol-DDT solution, the solubility of DDT in the methanol-water mixture decreased, creating a supersaturated solution and causing the DDT to precipitate from the solution. The p,p′-DDT can then be separated using filtration or centrifugation and be shipped to an incinerator for destruction. The amount of water required to yield precipitation is large. Table 6 shows the amount of water required to cause precipitation for single-component saturated pesticides solutions.

When water was added to the methanol extract of the pesticide contaminated soil, a stable micro-colloidal suspension was formed that was impossible to separate using conventional methods. Efforts to break the suspension by adding cationic polymer flocculants (Nalcolyte 7134, 7135, 7157), changing the pH (2 to 12) or centrifuging (up to 10000 g) were not successful.

TABLE 6. Approximate Solubility of Pesticides in Methanol at 25°C and the Amount of Water Required to Start Precipitation of the Pesticide

Pesticide	Solubility mg/L	Precipitating water amount (g water/g Methanol)
p,p′-DDT	26,000	0.56
Aldrin	16,000	0.4
Dinoseb	20,000	0.3
Endrin	14,000	0.15
Toxaphene	Slightly soluble	Not Available

Evaporation

Evaporation was used to separate the methanol-pesticide solution and concentrate the remaining methanol, water, and pesticide into a much smaller volume. A rotary evaporator (Fisher Scientific 09-548-105F) was used at 66°C to distill methanol from the water/pesticide mixture. Evaporation reduced the extract volume 30 times and no pesticide was detected in the condensate. Evaporation, therefore, would be an effective solvent recycling method for solvents with a wide range of contaminant concentration.

Granular Activated Carbon

Granular activated carbon (GAC) has been shown to be an effective method in removing organic contaminants from water or gas streams [*22*]. However, the adsorption of most organic compounds on GAC is less from an organic solvent than from an aqueous solution. This is because of the high solubility of pesticides in the organic solvents and the adsorption of some solvents onto GAC [*23*]. However, solvents like methanol, that have small, polar organic molecules are not easily adsorbed [*24*]. Studies were conducted to determine the adsorption of pesticides on GAC and the influence of carbon dosage, adsorption time, initial concentration, and solvent compositions at adsorption equilibrium.

The experimental procedure consisted of placing 200 ml of a pesticide/methanol mixture into a flask containing 2 g of activated carbon (10 g/L). Samples were collected from the mixing flask at different time intervals and the entire experiment was replicated three times. Figure 8 shows the removal of p,p′-DDT, p,p′-DDD, and p,p′-DDE as a func-

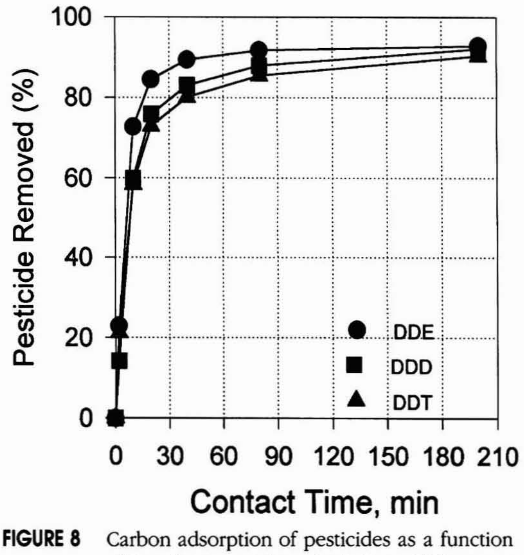

FIGURE 8 Carbon adsorption of pesticides as a function of time from a methanol solution of 80 mg pesticide/g of carbon.

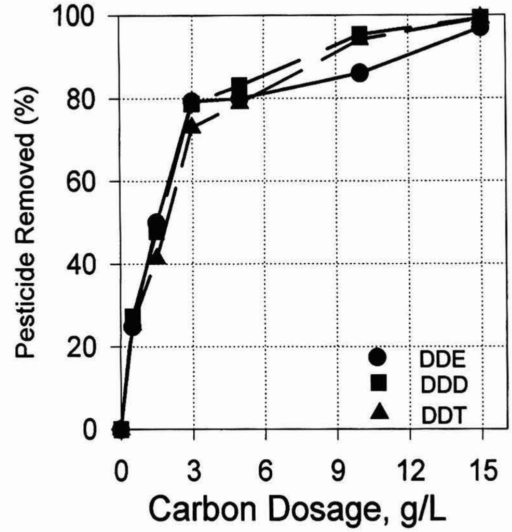

FIGURE 9 Pesticide adsorption as a function of carbon dosage.

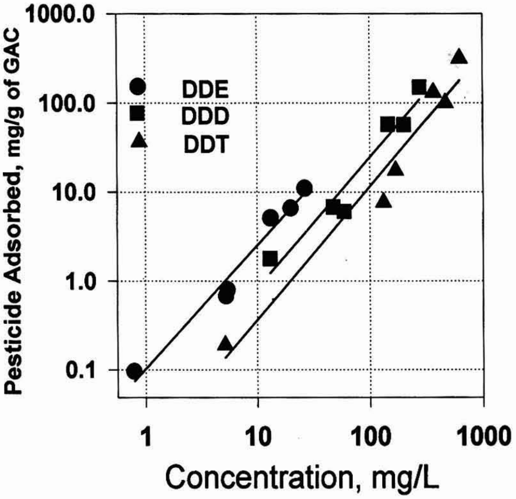

FIGURE 10 Carbon adsorption isotherms of p,p′-DDT, p,p′-DDD, and p,p′-DDE in a methanol solution. Single component Fruendlich constant, 1/n = 1.81.

tion of contact time. Activated carbon studies on removal of pesticides from methanol have shown that it is capable of reducing the concentration of these pesticides by more than 90% in less than 30 minutes.

The experiment conducted to determine the effect of the carbon dosage consisted of placing 200 ml of pesticide/methanol mixtures (50 mg/L DDE, 199 mg/L DDD, 503 mg/L DDT) into flasks that contained a specific concentration of carbon (0.5, 1.5, 3, 5, 10, 15 g/L). The mixture was stirred using a magnetic mixer for 24 hrs before samples were collected for analysis. Figure 9 shows the removal of pesticides from the methanol mixture as a function of carbon dosage. The data from these two experiments was rearranged to determine if the observed adsorption characteristics followed the Freundlich adsorption isotherm equation. Figure 10 shows the mass of pesticide adsorbed per gram of carbon as a function of pesticide concentration. The linear relationship between the log pesticide concentration and the log of the pesticide adsorbed confirmed that adsorption characteristics are in agreement with the Freundlich model. Since the tests indicate a large quantity of GAC is required (15 g/L) to remove pesticides from methanol, carbon adsorption may not be a cost effective method to remove pesticides from the solvent.

Synthetic polymeric adsorbents, such as Amberlite XAD-4, have shown to be equally effective in removing pesticides as carbon and could be regenerated more economically [*25*]. Experimental studies are needed to evaluate the use of synthetic adsorbents for the recovery of contaminants from methanol mixture.

Solvent Stripping

Liquid-liquid extraction is another effective method of regenerating solvents. Hexane can be used as a stripping solvent because the ratio of the concentration of organochlorine contaminants to hexane and methanol is about three. Hexane also has a lower density, creates no emulsion with methanol, and has a lower heat of vaporization (80.48 cal/g) compared to that of methanol (262.79 cal/g). However, hexane and methanol have some miscibility. When a small amount of potassium sulfate, 20 mg/L, and 10% water was added to the methanol-pesticide mixture prior to hexane addition, the two phases were found to be immiscible. As a result, the partitioning coefficient of the pesticides was increased, favoring hexane.

Solvent stripping of organics from an acetone mixture using kerosene has also been shown to be an effective method [*26*]. Although solvent stripping is technically feasible, preliminary equilibrium studies indicated that solvent stripping is more costly than evaporation since three volumes of hexane were required for every volume of methanol to remove 99% of the pesticides from the soil extract.

Post Treatment

The soil can be washed with water to remove the methanol before being returned to the site. An alternative treatment is to destroy the residual methanol using solid phase bioremediation, or volatilizing the remaining solvent. The highly concentrated waste may be destroyed by chemical oxidation or incineration. None of these treatment options were investigated during this study.

CONCLUSIONS

1) Solvent extraction has been shown to be a reliable and an effective method to remove pesticides from contaminated soils. A single-stage solvent extraction using either methanol or 2-propanol can successfully remove 65 to 75% of DDT, DDD and DDE from contaminated soils; whereas, a six stage extraction can remove $\geq$99%.

2) The main process parameters that affect the extraction efficiency of pesticides is the number of extraction stages and the total amount of solvent used. The high solubility of the pesticides in methanol resulted in rapid extraction rates

with the system reaching equilibrium in about thirty minutes. Lower L/S ratio (~1.6), short extraction periods (< 30 min.) and multiple extraction stages (4 to 6) were sufficient to achieve the cleanup goals. Optimum process variables have to be selected for a particular waste matrix to achieve residual concentration levels.

3) Moisture within the soil may reduce the extraction efficiency. However, when multistage extractions were used, the hydrophilic solvent dehydrates the soil during the first extraction cycle and the effects of moisture are minimal for the subsequent extraction stages.

4) The cost effectiveness of the solvent extraction process is affected by the solvent recycling method. Evaporation of the solvent is a very effective way to concentrate the contaminant. At low concentrations removal using GAC may be effective. The cost to recycle the amount of solvent generated by a four stage solvent extraction process (L/S = 2) using GAC was estimated to be approximately $47/ton of soil. However, the large amount of carbon needed to achieve 99% removal could be cost prohibitive. Separation using water to precipitate pesticides from soil extracts was shown not to be feasible due to the formation of a stable colloidal suspension.

Acknowledgment

This research was supported in part by an appointment to the Postgraduate Research Program at the National Risk Management Research Laboratory. The program is administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and the U.S. Environmental Protection Agency.

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Authors

Titles

Subjects

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Stephen R. Smith, Managing Director, Publications.

ENVIRONMENTAL PROGRESS

Author's Guide

Environmental Progress publishes papers on all aspects of environmental concern, with an emphasis on operating processes and engineering solutions to environmental problems. Much of the journal content is directed at the practicing chemical engineer who has environmental management responsibilities in one or more of the environmental media (air, water, and solid waste streams).

Most papers considered for publication deal with the problems, controls, and solutions associated with air and water pollution control, solid and hazardous waste management, and resource conservation (including recycle and reuse). Especially of interest are those papers containing engineering design and/or operating data and utilizing a multi-media approach. Papers dealing with regulatory requirements and/or public issues as they pertain to the chemical process industries are also of interest. Although the primary emphasis of the journal is, as noted, directed toward chemical engineering solutions, topical research papers on fate and effects research, environmental impacts, and innovative waste treatments are also published in limited numbers.

Authors are encouraged to submit papers that have not been presented at an AIChE meeting. These manuscripts are considered equally with papers presented at AIChE meetings.

Environmental Progress articles are typically no longer than 16 manuscript pages (double-spaced), including tables and figures. Generally, articles are published in order of acceptance (with some exceptions for balance) and can be expected to appear in print within six to nine months of acceptance (based on the current backlog). A decision regarding publication normally can be expected within two months. All submissions are first reviewed by the editor; those papers being considered for acceptance go on to a review by one or more members of *Environmental Progress'* Editorial Advisory Board and/or other peer reviewers.

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Papers should be sent directly to the editor of *Environmental Progress:*

Dr. Gary F. Bennett
Editor, *Environmental Progress*
Chemical Engineering Department
The University of Toledo
Toledo, OH 43606

Authors should submit three hard copies of the paper. Original figures should *not* be sent initially.

After review and upon acceptance for publication, the author will be directed to send his/her paper to AIChE's manuscript center, complete with original figures. The author will also be asked to complete a copyright transfer form and return it to New York. The accepted paper plus a signed Transfer of Copyright Agreement form should be directed to:

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Simultaneously, a copy of the paper and copyright form should be sent to the Editor.

FORMAT

Papers need not follow any specific format, but they should be written in a manner designed to best illustrate the material being presented. Appropriate use of headings and sub-headings does normally enhance a paper. A short review of the literature with appropriate references should also be included.

ABSTRACTS

Each paper should have an abstract of 100-200 words. The abstract should be a brief and factual account of the contents, conclusions, and relevance of the findings of the paper with an emphasis on what readers will gain from the manuscript.

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For style, please see *Chemical Engineering Progress'* Reference Style Guide which is available by request.

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Although not required, AIChE encourages authors to submit computer discs with their manuscripts. Although most word processing formats are acceptable, Mac-compatible material is preferred. Graphics are preferred in EPS, TIFF or PICT format. Your cooperation in complying with this request would be appreciated.

CONCLUSION

Attention to the details listed above will expedite editing and printing and increase the readability of your paper in *Environmental Progress.*