ENVIRONMENTAL PROGRESS

Vol. 13 No. 2 MAY 1994

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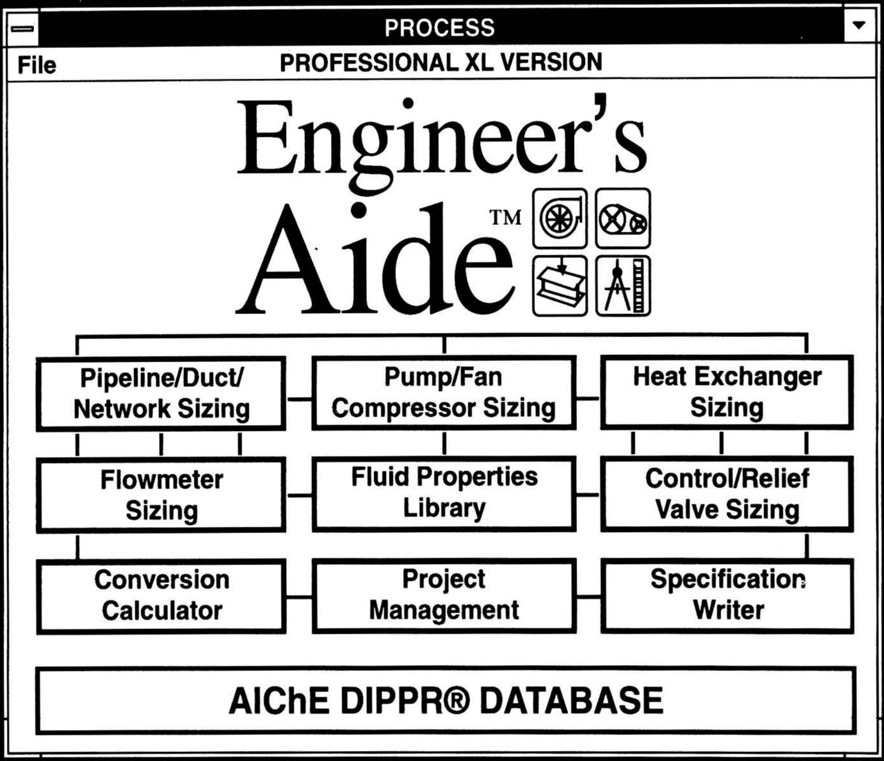

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Environmental Progress is a publication of the American Institute of Chemical Engineers. It will deal with multifaceted aspects of the pollution problem. It will provide through coverage of abatement, control, and containment of effluents and emissions 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.

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 $150. AIChE Environmental Division Members $29 included in dues. Outside the U.S. please add $12 per subscription for postage and handling. Single copies $45. Outside the U.S. please add $3 for postage and handling. Payment must be made in U.S. dollars. Second-class postage paid at New York, N.Y. and additional mailing offices.

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Cover: An aboveground bioremediation project at a Netherlands refinery where air movement was regulated (See page M5). Photo courtesy of Groundwater Technology Inc., Norwood, Massachusetts.
Cover Design: Joseph A. Roseti

Environmental Progress fee code: 0278-4491/93 $3.00. Postmaster: Please send change of addresses to Environmental Progress, AIChE, 345 E 47th Street, New York, N.Y. 10017.

Don't Do It!

An Alternative Approach to the Management of Oil Spill Cleanup

William B. Katz
523 Cherry Lane, Glenview, IL 60025

Would it shock you to know that some experts in the field think that trying to clean up an oil spill isn't such a good idea? That the damage to the world's environment caused by clean-up activities can exceed the damage caused by the spill itself? Unfortunately, it probably isn't possible in today's environmentally conscious society to just ignore an oil spill. For one thing, a large spill such as the Exxon Valdez accident in Prince William Sound is *big* business! Almost everyone involved in any way with a large oil spill stands to gain monitarily, with the exception of the company responsible for the spill plus its stockholders, and perhaps the taxpayers!

Those adversely affected by the spill are outraged. Their livelihood has been taken away, their magnificent scenery has been ruined and their accustomed mode of life has been disrupted. Their recompense may be long delayed, but may in the end compensate them well in money for their discomfort, replace old with more modern equipment and provide high paying jobs as part of a cleanup effort.

Environmental organizations cry out against a technological society that permits such disasters to occur. Despite much truth in their declarations, they gain valuable publicity. They also increase their membership and donations to fight the good fight against the "despoilers of the earth." The news media have a field day, gaining readers and viewers as their highly paid commentators update the public on day-to-day effects of the spill. Guest "experts" become public figures, increasing their salability for future assignments and consulting contracts.

William B. Katz founded the Illinois Chemical Corporation in 1964 and retired as President in 1990. He is currently Vice-President and Director of Environmental Site Assessments, National Environmental Management Group. He also teaches part-time at Oakton Community College, DesPlaines and Roosevelt University, Arlington Heights, Illinois. In 1975 he was a founding member of Committee F20 of ASTM and he served as Vice Chairman of Oil and Hazardous Spill Response until 1990. He is a registered Professional Engineer and a Fellow of AIChE.

Cleanup contractors and suppliers of equipment and materials from around the world compete fiercely for the suddenly available pot of gold. A big spill pours a breath of new life into an economically erratic business arena. Politicians gain valuable exposure to their constituencies as they struggle to assess blame and to promulgate new improved legislation to prevent such disasters from ever again occurring. Scientists and consultants accumulate masses of data that provide the impetus for papers and research projects for years in the future. Regulatory authorities, both State and Federal, gain new appropriations to buttress diminished, often overworked, staffs. The legal fraternity is overjoyed at the prospect of years of expensive litigation.

There's no doubt about it. Big oil spills are good for business! An important question is whether that business is good for the environment!

It has become increasingly clear to those directly involved in alleviating the impact of large spills that cleanup effectiveness is generally not very good. Those with real expertise are rarely allowed to make decisions based on their experience. More often decisions on what to do and how to best do it are made in the face of conflicting opinions by inexperienced officials beset by pressure from public opinion. Decisions are apt to be made for political expediency as much as for technical soundness.

The result of this mode of decision making is that often more environmental damage is done than if the clean-up were attempted by another method or in some other place than the chosen area.

Managing an oil spill is always a matter of tradeoffs. Even when the experts are allowed to make the decisions, something that often doesn't happen, opinions differ depending on the experience and background of the decision makers. Allowing a spill to remain on the surface of the water and perhaps to reach a shoreline puts birds and mammals at risk. Dispersing that oil into the water removes the risk for the most part, but may affect fish and other aquatic organisms adversely.

Cleaning a rocky shoreline with high pressure heated water may remove the danger that animals walking the shoreline become oil covered. However it may kill the small creatures inhabiting the intertidal area, that are a valuable and necessary part of the food chain supporting the larger animals. Trampling through a salt marsh to remove oil soaked vegetation may damage the marsh so badly that it cannot recover for years, if ever.

Experiences like these suggest that perhaps efforts to clean up oil spills should be greatly diminished. But there is another reason suggesting that perhaps there should be no effort made at all. This is an option that is rarely discussed or even considered.

From the viewpoint of the entire world an oil spill, even a very large one, is a local event. If left alone the damage from a spill will gradually be healed by naturally occurring processes. The oil will slowly be broken down by bacterial action. Vegetation will eventually reestablish itself. Displaced organisms will gradually return to the distressed area. This natural cleanup process may take a number of years but that is a very short time in the world's history. That is exactly what happens with naturally occurring oil seeps and with other "disasters" such as forest fires, volcanic eruptions and floods. Many people may be affected, economic loss may be huge, but cleanup of the environment occurs naturally. The Amoco Cadiz spill on the coast of Brittany a decade ago is a good example of this natural cleansing process.

The overall impact on the world's environment of a massive oil spill cleanup effort may be far more severe, though much more diffuse and thus harder to assess, than letting Nature provide the cleanup. Obviously there are some measures that should be taken during a massive oil spill. Recovery of concentrated crude, such as was accomplished by pumping off the unspilled oil from the Exxon Valdez, is both practical and fairly efficient, though a dangerous undertaking. Using floating barriers (called booms) to protect sensitive areas such as fish hatcheries or beaches or water desalination plants (as was done in the Persian Gulf) can reduce the impact of the spill in some instances.

Smaller spills, especially those from leaking underground storage tanks, have the potential to contaminate groundwater and hence potable water supplies. In such instances remediation may be necessary. But many spills are routinely cleaned up simply because it is present policy to do so. Little effort is made to determine the alternative environmental benefits to the Earth if one were to clean up a spill or leave it alone.

It is obvious that much of the tremendous expenditure of money for oil spill cleanup is wasted because recovery efficiencies are extremely poor. Also, damage to the environment from cleanup activities usually adds to the overall impact of the spill rather than mitigating it.

Perhaps it would be far better to establish a schedule of severe fines for spilling oil, to provide a high incentive for prevention of spills. The money collected from such fines could and should be used to alleviate the distress caused by the spill. It might also be used to fund research and development on alternative, non-polluting sources of energy. This situation is a challenge to everyone concerned with the environment. We must do our best to reduce the number of oil spills that occur. In the United States alone there are several thousand reported every year, both on land and on water; most of these are small. Such cleanup as is conducted is handled as efficiently as possible by a well organized and technically proficient industry.

Oil spills will occur as long as a major portion of the world's energy needs is supplied by burning oil. Increased attention to prevention may reduce the number, but accidents cannot be legislated out of existence. The real challenge is to develop alternative sources of energy and eliminate our dependence on oil. Until that happy day arrives, we should leave oil spills alone.

AIChE Superfund Task Force Issues Position Paper on CERCLA

The American Institute of Chemical Engineers' (AIChE's) Government Programs Steering Committee is urging Major changes to the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), commonly known as Superfund. Superfund requires that the US Environmental Protection Agency determine the nation's most serious abandoned polluted sites and gives the agency the power to force those responsible to clean the sites. The recommendations, developed by a Superfund Task Force and contained in a new position paper, *An Engineering Approach to Superfund Clean-ups*, are being issued as Congress prepares for the debate on Superfund's reauthorization this year.

In the paper, the task force says that, although well-intentioned, CERCLA "is not meeting expectations." "Clean-ups are too slow, cost too much, and are unfair as to who pays," the task force found.

The report adds that "CERCLA clean-ups could be done more efficiently and quickly and at significantly lower cost...if an engineering-based, outcome-oriented approach were adopted." That approach "places much greater emphasis on expediting site clean-ups in order to reduce as quickly as possible the risk to human health and the environment, rather than on the administrative compliance that is the hallmark of the current process." The task force has concluded that the bottom line is that "CERCLA needs to be reformulated to focus on results rather than process."

Using site-specific risk assessment based on realistic assumptions, and taking into account the intended future use of the land, would be a first step. The task force also recommends compressing the multiple site evaluation process into a single feasibility study, and devoting more resources to developing and implementing innovative and cost-effective technologies. It also stresses the importance of community involvement.

The task force cautions, however, that even a more rational, technological approach, while improving CERCLA, will not solve all of the act's problems. "It is impossible to fix CERCLA so that it conducts clean-ups quickly, efficiently, and cost-effectively without fixing the liability system," the report warns. "A liability system that...does not delay clean-ups or disproportionately absorb clean-up resources" is what's needed, along with "strong disincentives for failure to resolve liability issues quickly."

According to Dale Brooks, AIChE's managing director of government relations, the new policy paper is intended to assist policy makers reach important decisions on amending the Superfund law by providing background information and technical assessments. "We developed this position paper because Superfund affects our membership, perhaps more than that of any other professional group" Brooks said.

The nine-member Superfund task force was chaired by Peter Lederman of the New Jersey Institute of Technology. Members included Bill Byers, past chair of AIChE's Environmental Division; former AIChE President Stanley Proctor; and J. Winston Porter, president of the Waste Policy Center, who, as deputy administrator of the US Environmental Protection Agency, oversaw the Superfund program from 1985-1989, and has recently written about it for The New York Times and the *Wall Street Journal.*

If you would like a copy of the position paper please call AIChExpress FaxBack at 212-705-8300 and request document 8200.

Environmental Industry Continues to Experience Slow Growth

Farkas Berkowitz & Co., a Washington, DC, environmental management consulting firm, recently presented its sixth annual "State-of-the-Industry Report" as the opening keynote address before an audience of environment industry executives at Environmental Business '94. The firm reviewed the financial performance, trends and outlook for environmental consulting, remediation, analytical and off-site hazardous waste management services in the U.S.; plus an overview of the environmental industry worldwide.

Evaluating 1993 results, they reported that nearly every sector showed clear signs of maturity that had been masked by the 1990-91 recession and the subsequent slow-growing economy. The U.S. market continues to experience slow growth, modest profitability, and tougher competition brought on by overcapacity. The $9 billion environmental consulting and engineering market showed no growth in 1993, continuing a steady six year decline. "The remediation market was also flat, with increased demand offset by decreased prices," according to Mr. Farkas. Commenting on the $ 1.5 billion analytical services market, Dr. Berkowitz said, "Prices have been falling by 5 to 10 percent each year since 1990, and the trend accelerated in 1993." She continued, "The $3.2 billion market for off-site treatment and disposal of hazardous wastes declined almost 4 percent in 1993, and will never return to the peak growth rate of 24 percent seen in 1990, when the first set of land ban regulations took full effect." Dr. Berkowitz observed, "Maturity stimulates pursuit of global markets, and although expenditures for environmental services are lower in other countries than in the U.S., projected growth rates are two to three times higher.

Comparing 1993 with 1992 for the Farkas Berkowitz composite index of 17 publicly traded environmental consulting firms, accounting for 20 percent of the market, Mr. Farkas said, "For the group as a whole, revenues were flat and operating earnings were up by 8 percent." He went on to remark, "Growth and earnings varied substantially among the index firms. five had good growth of over 14 percent; five saw revenues decline by more than 3 percent. Profits declined for more than half of the index firms, and average operating margins based on gross revenues slipped to 3.2 percent.

The State-of-the-Industry Report will be available for purchase by mid-April. Those wishing to purchase the report should send a check for $150 to Farkas Berkowitz & company, Attention Julia Yurwitz, 1220 Nineteenth Street, NW, Suite 300, Washington, D.C. 20036. Telephone inquiries are welcome at (202) 833-7530.

On-Site Bioremediation of Contaminated Soils Successful at Dutch Refinery

Aboveground bioremediation applied in engineered treatment cells is being used at a Rotterdam, Holland, refinery for efficient treatment of petroleum contaminated soils to low residual levels as specified by stringent Dutch regulations. Soils will be remediated to these levels within nine months, and may then be reused on-site.

According to Project Manager Yvo Veenis of Groundwater Technology Inc., Norwood, Massachusetts, the refinery's remediation consultant "Treating soils on-site will be accomplished at about half the cost of off-site treatment alternatives. In addition, the refinery will avoid the liability of transporting contaminated soils on public roads and the limited applications for soils treated by destructive processes."

Aboveground bioremediation involves placing soils in engineered treatment cells or "biopiles" which contain manifolded piping systems for oxygenation, nutrient addition, process control and monitoring. The nutrients and increased oxygen stimulate the growth of naturally occurring bacteria that degrade the hydrocarbons to carbon dioxide and water. The process is controlled by air pumping equipment which regulates air flow and vapor systems which treat off-gases (See photograph on the cover of this issue). The treatment cells are contained within an impermeable base and protective sheeting which prevents run-off and traps heat during cold periods.

To obtain regulatory approval for using bioremediation cells to treat the soils, a pilot study was conducted to demonstrate the applicability of the process for this site. The pilot test was a success and the refinery was given permission to treat and reuse larger quantities of contaminated soils on-site.

This project reconfirms the efficacy of engineered biotreatment of cells for treating petroleum contaminated soils at costs significantly lower than off-site treatment and disposal.

For more information please contact Groundwater Technology Inc., 100 River Ridge Drive, Norwood, MA 02062.

Washington Environmental Newsletter

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

Is chlorine an "evil element" whose use should be totally eliminated? Or is it a critical chemical building block in products that enhance the quality of life? In the coming months, the U.S. Congress may be forced to chose sides in this emerging debate.

On January 31, the U.S. Environmental Protection Agency released "President Clinton's Clean Water Initiative." The Administration's initiative stated:

> *To develop a strategy to comprehensively protect human health and the environment and to move towards the national goal of the Clean Water Act of eliminating the discharge of toxic pollutants, the Administration will develop a national strategy for substituting, reducing, or prohibiting the use of chlorine and chlorinated compounds.*

As part of this effort, EPA would convene a task force of Federal agency representatives and outside experts to "assess the use, environmental and health impacts of chlorine and chlorinated compounds, and the availability and relative efficacy and safety of substitutes for these substances" as used in drinking water systems and wastewater treatment, solvent production, PVC and other plastics fabrication, and pulp and paper manufacturing. The EPA Administrator would then review the information collected by the task force and release the national strategy for substituting, reducing, or prohibiting the use of chlorine and chlorinated compounds.

The Administration's proposal has been adopted by Senator Howard M. Metzenbaum (D-OH). Sen. Metzenbaum announced his intention to incorporate the proposal as an amendment to a bill (S. 1114) to reauthorize the Clean Water Act. Although he did not offer the amendment when the bill was approved by a Senate committee in February, he is expected to attempt to offer it when the bill goes before the full Senate later this year.

A similar proposal has been introduced by Rep. Bill Richardson (D-NM) in the House of Representatives. H.R. 2898, the "Chlorine Zero Discharge Act," would require EPA to prepare a report on industrial discharges into water of organochlorine compounds and their byproducts and metabolites. The report would be required to "contain recommendations for achieving a zero discharge policy for important categories of organochlorine pollution sources."

THE USES OF CHLORINE

When the general public thinks about chlorine, household laundry bleach, swimming pool disinfecting, and drinking water purification are most likely to come to mind. In reality, chlorine is utilized in 15,000 commercial compounds sold in the U.S. Chlorine ranked tenth in 1992 U.S. chemical production at 22.3 billion pounds.

Chlorine and chlorinated compounds are used, directly or indirectly, in 98% of U.S. drinking water systems, 85% of pharmaceuticals, and 96% of crop-protection chemicals. They are also widely used in plastics, petroleum refining, paper manufacturing, disinfectants, flame-retardant materials, dry cleaning, food processing, paints, refrigerants, insulation, wastewater treatment, and many other industrial processes and products.

An independent study prepared for the Chlorine Institute estimates that 1.3 million U.S. jobs, generating more than $31 billion in wages and salaries, depend on the chlorine industry. Almost 40% of all U.S. jobs and income depend in some way on chlorine and the products of the chlorine industry. Chlorine-based products represent a nearly $3 billion net trade surplus. The study also estimates that chlorine and chlorinated compounds save U.S. consumers more than $90 billion annually — $1,440 for every family of four — compared to alternative products or processes.

HEALTH EFFECTS OF CHLORINE

Chlorine compounds have a broad range of chemical and physical properties that govern their behavior in the environment. Some chlorinated compounds, such as dioxin, PCBs, and DDT, have been identified as presenting risks to human health because of their persistent, bioaccumulative, and toxic natures. These substances have been linked to reproductive, developmental, and neurological impairment, cancer, birth defects, immune suppression, and damage to the liver and kidneys. There is no authoritative study, however, linking the entire class of chlorine compounds to adverse health effects.

THE CLINTON ADMINISTRATION AND CHLORINE

The Clean Water Initiative was not the first time the Clinton Administration had weighed in on the chlorine issue. In July of 1993, the Administration unveiled a draft Executive Order on "environmentally preferable products" that proposed a ban on the purchase by the Federal Government of paper bleached with chlorine. After receiving public comments and conducting a review of the issue, the Administration backed off the proposal. Instead, President Clinton instructed Federal agencies to increase their purchases of recycled paper and directed that the brightness specifications for paper be revised to allow the purchase of stationery produced without chlorine bleaching.

The Administration's proposal for a national strategy on chlorine and chlorinated compounds appears to the be the result of a report of the International Joint Commission, a U.S.-Canadian agency that monitors and assesses progress on the implementation of an agreement between the two nations on water quality in the Great Lakes. In October of 1992, the International Joint Commission recommended that the use of chlorine and chlorinated compounds be phased out. In response, EPA stated: "The United States does not support sunsetting all uses of chlorine and chlorine-containing compounds ..., rather the U.S. has chosen to pursue a weight-of-evidence approach ... (to address) specific chlorinated compounds that exert deleterious and wide-spread environmental impacts." The proposed national strategy in the Administration's Clean Water Initiative appears to be at odds with the EPA's position on the commission's recommendations.

RESPONSE TO THE ADMINISTRATION'S PROPOSAL

The proposed national strategy has been endorsed by the Environmental Defense Fund, Greenpeace, the National Wildlife Federation, and the U.S. Public Information Research Group. The National Wildlife Federation called chlorine an "evil element" that should be banned. Greenpeace stated that phasing out the use of chlorine could save billions annually in chemical, energy, and water costs, create new jobs, and stimulate more effective and productive industrial processes.

The response from industry to the Administration's proposed national strategy on chlorine has been swift and forceful. The Clean Water Industry Coalition, an ad hoc group of companies and trade associations interested in the pending Clean Water Act reauthorization, called the Administration's proposal "deficient" and "unscientific." The National Agricultural Chemicals Association wrote to Carol M. Browner, Administrator of EPA, saying: "To propose eliminating chlorine and chlorine compounds from daily commerce is to suggest that the federal government can and should rearrange the periodic chart of the elements."

The Chemical Manufacturers Association called the proposal "outrageous, unnecessary and unfounded." It charged that "[t]he proposed initiative ignores existing laws and regulations that provide the basis for determining appropriate restrictions on the discharge (not the use) of chlorine and chlorine-based chemicals, taking into consideration economic, environmental, and technological factors". CMA proposed that chlorine and chlorinated compounds be evaluated through a process based on: (1) a scientifically credible risk assessment of the specific compounds and their potential alternatives; (2) a fair and balanced process involving all stakeholders; and (3) an evaluation of social and economic factors.

Seventy-five members of Congress wrote to the President in March about their concerns with the Administration's chlorine proposal. Stating that they do not support the proposed study and national strategy, the members told the President: "To ban the use of an entire class of compounds based on the problems associated with only a few is scientifically unfounded. It further sends a message to the public that all chlorine compounds and products of chlorine chemistry present unacceptable risks from their responsible use and release. This premise is simply not true and will be disastrous to the U.S. economy and the public's well being."

AIChE ACTION

AIChE's Government Programs Steering Committee has directed the establishment of a chlorine task force to ensure that the views of chemical engineers are adequately considered as Congress debates this issue. In addition, AIChE's Washington staff has been attending meetings and briefings with other groups interested in the issue in order to keep AIChE's membership fully informed.

AIChE's Government Relations staff may be contacted at : 1300 I St., N.W., Suite 1090, East Tower, Washington, D.C. 20005. Telephone (202) 962-8690 • FAX: (202) 962-8699

New Separation Chemistry Techniques for Radioactive Waste and Other Specific Applications, L. Cecille, M. Casarci, and L. Pietrelli editors, Elsevier Applied Science, New York, NY (1991) 307 pages [ISBN No: 1-85166-656-7] U.S. List Price: $ 102.00.

This book includes papers presented at a technical seminar jointly organized by the Commission of the European Communities (CEC), Directorate-General for Science, Research and Development, and the Italian Commission for Nuclear and Alternative Energy Sources (ENEA). It examines the current state-of-the-art technology for the separation of various metal ions from mixtures, with an emphasis on the separation of radionuclides from radioactive waste. The seminar was comprised of five technical sessions, each devoted to the discussion of the merits of one family of new extractants, exchangers, and absorbers.

The Opening Session section provides an overview on new separation chemistry techniques and their potential application to processing radioactive wastes, reduction of radioactive discharges, reduction of waste volumes, isolation of long-lived alpha and beta emitters, recovery of valuable metals, and other nonnuclear applications. The TRUEX (transuranium extraction) process, developed at Argonne National Laboratory, is described in detail by its developers (Horwitz *et al.*).

Section I examines the use of various amine/amide based extractants on several metal cations. The extracted species include alkaline earths, uranyl and other radioactive actinides, and the platinum group metals. One of the merits of amide-based extractants pointed out in this section is that they are incinerable without giving rise to ash production.

Section II discusses bidentate organophosphorus-based extractants, exchangers, and absorbers for removing actinides, lanthanides, and other metal ions from liquid waste. The application of octylphenyl-N,N-diisobutylcarbamoyl-methylphosphine (CMPO) to several systems is reported. A new bidentate type named TRPO (trialkyl phosphine oxide) has been demonstrated to be a good competitor for CMPO.

Sections III and IV cover the application of cyclic phenol-formaldehyde condensates or calixarenes and crown-ethers as complexing agents. A successful application of calixarenes was reported which dealt with selective complexation of rubidium in human blood.

Sections V and VI cover other types of extractants (macrocyclic ligands, alkylpyridinium nitrates, and phosphomethyl substituted phenols)and ion exchanger/absorbers.

This book serves as a good technical reference for what is current in the field. The very selective extractants synthesized recently as well as the new separation techniques reported offer promising prospects in the field of separation science and analytical chemistry. This book is suited to those already working in the area of advanced separation of metals from liquid wastes.

John F. Schneider
Energy Systems Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

Response Manual for Combatting Spills of Floating Hazardous Chemicals, A. Szluhla, D. Allen, P. Dalfonso, C. Heckman, I. Moisson, S. Moore, A. Morrison, W. Nicholas, and J. Summers, Noyes Data Corporation, Park Ridge, NJ (1992) 436 pages [ISBN No: 0-8155-1292-9] U.S.List Price: $ 64.00.

This manual, written by members of the Maxime Corporation, Oak Ridge, Tennessee, provides information on methods for combatting spills of more than 300 floating chemicals. Originally written for the U.S. Coast Guard (USCG), the manual outlines a logical decision-making process designed to lead one to the most appropriate response methods to be used with the chemical spilled. This procedure is consistent with the requirement of the NCP, CERCLA, and RCRA (for disposal).

Information is given so that an on-scene coordinator will be:

- Aware of the hazards posed by the spilled chemical, and
- Informed of the limitations of the response methods.

The manual has two parts, resulting from the combination of two separate reports from the USCG. Part I covers methods for responding to spills of floating hazardous chemicals; Part II covers the classification of floating chemicals.

The titles of the various chapters reveal the manual's content:

- Decision-Making Process
    - Spill characterization
    - Decision analysis
    - Implementation
    - Feedback
- Spill Isolation
    - In water
    - On land
    - Flow reduction technology
- Spill Mitigation and Removal Techniques
    - Vapor suppression
    - Removal techniques
    - *In situ* treatment technology
- Special Problems
    - Partially water soluble chemicals
    - Submerged sources
    - Night spills
    - Materials which rapidly form monolayers
    - Burning spills
    - Boiling liquid expanding vapor explosion
- Physical-Chemical Characteristics of Floating CHRIS Chemicals
- Evaluation of Spill Removal Equipment and Chemical Removal Technology
- Decision-Making Work Sheets
- Classification of Floating CHRIS Chemicals and State-of-the-Art Review of Containment and Recovery Technology
- Evaluation of Foam Vapor Suppression and Compatibility Between Spilled Chemicals and Response Equipment.

The aspects of the book I found most interesting and useful are:

- The list of hazardous chemicals - their properties, and compatibility with response equipment
- The case studies of selection response actions - good, although more detail and more case histories would be helpful

•The evaluation of foam suppression, for chemicals that vaporize present the most significant hazards and are hardest to control/mitigate. The 75 pages devoted to this topic are well-advised and well done.

Overall, this is a very useful book for spill response and one that potential on-scene coordinators will want to read thoroughly in advance of their on-scene tasks after a spill occurs. The book is not a manual to be consulted in an emergency unless one is thoroughly familiar with its contents.

Gary F. Bennett, Ph.D.
Professor Emeritus of Biochemical Engineering
Department of Chemical Engineering
University of Toledo
Toledo, OH 43606

Chemistry with Ultrasound, Vol. 28, Critical Reports on Applied Chemistry, Society of Chemical Industry,
T.J. Mason editor, Elsevier Applied Science, New York, NY (1990) 195 pages
[ISBN No: 1-85166-422-X]
U.S. List Price: $ 98.00.

The use of ultrasound for driving or enhancing chemical reactivity, called sonochemistry for short, is an area that is perhaps unfamiliar to most practitioners in environmental science and environmental engineering. This compact book provides a concise introduction to the field with good coverage of the physics behind sonochemistry, an overview of the types of reactions which have been enhanced with sonochemistry, and a discussion of the equipment required.

The sonochemical destruction of various organic materials in water has been recently demonstrated by a few research groups and it appears that sonochemistry may have a place as one of the advanced oxidation techniques available for environmental remediation or waste destruction in chemical plants. Thus far, the sonochemical destruction of methylene chloride, chloroform, carbon tetrachloride, perchloroethylene, 1,2-dichloroethane, trichloroethylene, 1,1,1-trichloroethan, benzene, toluene, nitrophenol, and ethylenediaminetetraacetic acid have been demonstrated in bench-scale systems. These results are encouraging. Back of the envelope cost estimates place this technology in the range of other advanced oxidation methods such as UV/ozone treatment. However, a great deal of development work remains to be done before a sonochemical method reaches the field. This book does not discuss those results, many of which were not published until this year. However, the book does provide the interested researcher or practitioner with the background information needed to interpret the available journal literature.

To place the interest of a book on sonochemistry into perspective for those involved in environmental work, I'll briefly describe how ultrasound affects chemical reactivity. The sonochemical effect is due to the action of cavitation bubbles and is essentially the same effect that causes cavitation erosion of impellers in pumps if cavitation is allowed to occur and the effect that is employed in small ultrasonic cleaners as may be found in most laboratories (and jewelry stores). During the sonication of a liquid, alternating cycles of rarefaction and compression occur. Cavities can form during the rarefaction cycle. For a pure liquid, the sonication intensity required to form cavities can be calculated in terms of the hydrostatic pressure and the vapor pressure of the liquid. In practice, lower intensities than are required for a truly pure liquid will produce cavitation. This is because dissolved gases and dispersed solids provide nucleation sites for the cavities to form. Once formed a cavity may grow with subsequent cycles of the sonic energy and become an "ordinary" bubble, floating to the top of the liquid. It may reach a stable, but small size (these are known as stable cavitation bubbles), or it may collapse after a few cycles while it is still very small (these are known as transient cavitation bubbles). The ordinary bubbles are of no interest in terms of sonochemistry. The transient bubbles are of greatest interest, for these bubbles collapse catastrophically and almost adiabatically to essentially zero volume. This results in the formation of microscopic spots of very high pressure and very high temperature. These conditions have both been estimated theoretically and measured to be in the vicinity of a few *hundred* atmospheres and a few *thousand* degrees Kelvin. Extreme conditions indeed! The stable cavitation bubbles also undergo compression and may have very high local temperatures and pressures, although not as extreme as those of the transient cavitation bubbles. The amazing feature about this effect is that these conditions exist microscopically in the liquid while the system as a whole is sitting at regular laboratory conditions.

This book contains five chapters which introduce the reader to the topic of sonochemistry. The first chapter is an introduction written by T.J. Mason which briefly covers the physics of cavitation, and discusses the influence of ultrasound on chemical reactivity. The last section of the chapter discusses several nonreactive ways in which ultrasound finds usage in chemical technology, in particular, in atomization, precipitation and crystallization, filtration, membrane permeation, and electrochemistry.

The second chapter, written by J. Lindley, discusses the effects of ultrasound on inorganic and organometallic chemistry. The effects of sonication on metals and metal crystallization are also discussed in this chapter. A large number of reactions are presented with an indication of the reactivity improvement provided by ultrasound. Many of the reactions, particularly those involving the formation of organometallic compounds, do not require high intensity ultrasound, but rather the low intensity sort which can be generated using a laboratory cleaning bath. Ultrasonication reduced the required reaction times by about an order of magnitude in most of the reactions cited. Lindley finishes the chapter by presenting the effects of ultrasound in catalysis. Here ultrasound can be applied both in catalyst preparation, where it reduces catalyst particle size with a concomitant increase in interfacial area, and in the final reacting system, where ultrasound can produce significant improvements in mass transport, the generation of active sites, and the desorption of products and poisons from catalyst surfaces.

The third chapter, written by R.S. Davidson, discusses ultrasonically assisted organic synthesis. It overlaps somewhat with the previous chapter in that many of the reactions cited involve the formation of organometallic species, however it covers a wide range of organic synthesis. Davidson includes a discussion of free radical and excited state generation by ultrasound. This is of particular relevance to the sonochemical destruction of dilute aqueous hazardous materials as one of the mechanisms for the sonochemical destruction of these compounds is free radical attack by hydroxyl and hydrogen radicals created from the solvent.

The fourth chapter, written by J.P. Lorimer, discusses the effects of ultrasound on polymers. Ultrasound can both promote polymerization and cause polymer degradation. It is also of use in polymer processing and ultrasonic welding of plastics. Ultrasound driven copolymerization of both polymer-polymer and polymer-monomer systems has been experimentally demonstrated by several investigators.

The final chapter, written by T.J. Goodwin, discusses the equipment required for the generation and delivery of ultrasonic energy. He describes both the available laboratory-scale equipment, such as ultrasonic cleaning baths, direct immersion probes, and whistle reactors, and larger scale sonochemical equipment which has been proposed. He notes that large scale equipment appropriate to sonochemical processing on a commercial scale is not at present readily available.

This book will be of value to individuals interested in learning more about the potential of sonochemistry for environmental applications or to the researcher just starting to explore those possible applications. The book should not be considered an encyclopedic reference on the topic, but rather an introduction and tutorial.

H. Michael Cheung, Ph.D., P.E.,
Associate Professor of
Chemical Engineering
Department of Chemical Engineering
The University of Akron
Akron, OH 44325-3906

Video Review

Hazardous Materials: The Chemistry of Hazardous Materials, A videotape produced by Air and Water Technologies, in association with Metcalf and Eddy, Somerville, NJ (1992) 20 minutes long, $495.00.

This videotape is relatively simplistic but provides an excellent discussion of basic chemistry with the purpose of laying the foundation for understanding the properties and hazards of chemicals.

The principal subjects discussed in this videotape are:

- Physical characteristics
  - Solid, liquid, or gas
  - Appearance and odor
  - Density, specific gravity, and vapor density
  - Viscosity
- Physical changes
  - Temperature effects: phase changes, sublimation, and evaporation
  - Solubility and concentration
- Chemical reactions
  - Stable and unstable chemicals
  - Compatibility and incompatibility
  - Corrosives (pH)
  - Flammability (UEL, LEL, and flash point)
  - Explosives
  - Oxidizers
  - Reactivity
  - Polymerization

In addition to the videotape, the following teaching aids are supplied:

- A suggested lesson plan
- A discussion guide
- Review questions and answers
- A sign-up form
- An annotated text
- Additional references

My opinion of the videotape is that it is very good, but a very fast and concentrated overview of what is taught in a basic chemistry course.

Most (assumimg the audience will be primarily non-college degreed workers) will need more time than the videotape permits to assimilate the material in it. I suggest two or more viewings of the videotape. In addition, the use of the textbook and its supplementary material will be helpful. I also suggest the Materials Safety Data Sheet be used in the review/supplementation session.

Overall I'd give the videotape high marks, however at a very high price compared to books. The latter contain far more information at a much lower price.

Gary F. Bennett, Ph.D.
Professor Emeritus of Biochemical Engineering
Department of Chemical Engineering
University of Toledo
Toledo, OH 43606

Environmental Resources on the Internet

Ashok Kumar and Ajay Manocha
Department of Civil Engineering, University of Toledo, Toledo, OH 43606

Introduction

Almost everyday we hear about the upcoming advent of the Information Highway. The Highway will be the next generation of the present-day networks such as the Internet. The Internet is a global web of computer networks. What that basically means is that these computers can exchange information amongst themselves. An electronic file or a software package available on one computer can be retrieved by a user on another computer, if the two computers are linked. The Internet spans all the continents of the world, and a good many countries in most of them. Given an Internet computer account, you could download ("download" is the term used to describe the process of transferring a computer file from a remote source into your computer) a file from an Internet location (also called a "site") in Holland, check the latest news in Japan, or go on down to Australia to check the weather, without leaving your desk.

Computers connected to the Internet contain vast amounts of information on a wide variety of topics. The amount of software and documents available *today* at a well stocked site is enough to keep you busy for a few years, and more information and software are being added every day. These computers are capable of data transmission at rates several orders of magnitude faster than the ubiquitous 2400 bps modem. The maximum theoretical rate of data transmission on the Internet today is 45 million bits per second, and although not all the secondary networks which make up the Internet can handle that speed, the transmission rates are high enough to make the Internet a valuable resource.

The information available is as varied as the people who upload it, and since the Internet boasts a dynamic community of users, the information, more often than not, is up to date. There are a number of sites that carry information of interest for the environmental professional. The information available includes regulations, standard test methods, case studies of environmental projects, software, contacts within government agencies, and more.

Apart from the information available at different sites, there are newsgroups available on a large number of topics, including environmental science. These newsgroups are electronic bulletin boards, where anyone can post their views, information or articles they find interesting. Since there are literally thousands of newsgroups, you can pick a newsgroup that matches your interests, and use it to communicate with other like-minded folk. However, the openness of the newsgroups is also a drawback when you are looking for quality information. It may be necessary for you to go through a number of postings before you find what you really need. An alternative is to use the mailing lists or LISTSERVS, which are available on a wide range of subjects. Upon subscription (free of cost), you will begin to receive periodic mailings to your E-mail (electronic mail) account. The mail will contain articles on the subject of that LISTSERV, compiled and edited by people who take their work seriously.

Another facility available on the Internet is easy access to other scientists and professionals in your field of interest who have E-mail addresses. You can exchange ideas, information and data with them at a fraction of the cost of regular mail, and at an almost unbelievable speed. For example, E-mail sent from the USA to Singapore can be delivered and acknowledged in a matter of minutes. This same speed also allows two users logged on at remote sites to have real-time "chats" through their computers.

However, since there is no adequate documentation of the information available at a particular site, the hunt for information can be a time-consuming process. The aim of the paper is to document the Internet-accessible sites that have information of interest to the environmental professional. The procedure to obtain access to the Internet and the available information is also described. The material presented in this paper can be used as a starting point in your search for information on the Internet.

Obtaining Acess to the Internet

There are a number of ways to obtain access to the Internet. Nearly all the universities in the United States and Canada currently provide full Internet access to all their students and faculty. A growing number of companies are obtaining Internet connections, and chances are that access is freely provided within the company. A number of cities in every state provide access through dial-in modems. In Ohio, Cleveland, Lorain, Medina and Youngstown have Freenet networks, through which you can access other sites. Table 1 lists the facilities available in North America. The numbers were taken from a year-old version of the *Big Dummy's Guide to the Internet* by Adam Gaffin. It might be a good idea to confirm the number before you dial in, or at least try to connect for the first time during the day (local time). The authors dialed a number on the list, and instead of a modem at the other end, they reached somebody's answering machine.

Even if none of the above sources are of any use to you (for example, you aren't in college anymore, your company doesn't have an Internet connection, and you live in a city with no public access to the Internet), there are a few companies (Delphi [1-800-695-4005], PSI [1-800-82PSI82] and CNS, Inc., [1-800-748-1200]) who will provide you with Internet connections for a subscription fee.

The rates for Internet access through the organizations listed in Table 1 vary considerably, and depend upon usage. Generally, the rates fall under the following headings:

1. Initial 'set-up' or 'sign-on' fees. This is a one time charge that the user pays on getting a connection. It varies from organiza tion to organization, and is generally around $50 or less.
2. The subscription fee. This is a periodic charge, and varies from $60 per year to $35 per month. Usually, the subscription fees also cover a fixed number of free hours per month.
3. Usage charges for time over and above are the 'free' hours (that come with the subscription). These rates are in the region of $2 to $8 per hour.

Almost all the organizations use a combination of the above three rate categories. In addition, there may be extra charges for some of the features that you use. Some companies charge for disk storage above a specified limit, or may have different rates for off-peak hour usage. The Freenets mentioned in Table I do not charge their users, and depending upon the time you spend on the Internet, the long distance phone charges may turn out to be more economical .

Once you have an account to use the Internet, an account name or user-identification and a password will be provided to you. Since you are generally charged by the hour if your access is through a private company, it is a good idea to keep your password to yourself, to prevent anyone else from using your account. Even if you are not paying for access, which is generally the case with university accounts, keep your password secret. Also, since a computer 'hacker' will try to use the account name as the password (a surprisingly large number of people use their account name as the password), it is important that you choose a different password.

After the user is logged in and has full Internet access, he/she should be able to use the following features:

1. E-mail
2. Telnet
3. FTP (File Transfer Protocol)
4. Gopher

E-mail and Telnet are available on all computer systems, while availability of FTP and Gopher varies from system to system. These are the tools that will allow you full access to anywhere in cyberspace you want to go.

Internet Sites

Numerous Internet sites today provide access to the public. The files at these sites deal with a large number of topics. Software for various applications is available for downloading. Given below are the three most used information-retrieval tools and the Internet sites with information on environmental topics.

1. Gopher:

Gopher offers access to a large amount of information at numerous sites, without the user needing to 'log on' at the site from which information is accessed. It is a fast and convenient way of accessing information on a particular subject. Due to the overwhelming amount of information available on the Internet, it is not feasible to list all the sites which carry files on topics related to the environment. However, two of the sites listed below have a stated aim of providing links from their sites to all environmental information available on the Net. The other gophers listed below provide resources on a broad range of subjects relating to the environment, ranging from scientific data to activist manifestos.

Envirogopher

This site is operated and maintained by the EnviroLink Network. The stated goal of the gopher is to ultimately provide access to all environmental information available on the Internet. In keeping with that goal, almost all the directory titles are pointers to other sites with environmental information.

Ecogopher

Ecogopher is run by the Division of Recoverable and Disposable Resources (DRDR). This gopher has much the same goals as EnviroGopher, *i.e.*, to provide access to all environmental information on the Net. A facility provided at this site is Keyword search of All The Information at Ecogopher, KATIE.

ERIN (Environmental Resources InformaVon Network)

This Australian site has information on endangered species, vegetation types, environmental monitoring, environmental protection, legislation, and more.

W.H.O. (World Health Organization) Gopher

The WHO gopher holds information on environmental health topics. Selected back issues of the Environmental Health Newsletter and of the International Program on Chemical Safety are available.

L.T.E.R. (Long Term Ecological Research) Gopher

This site holds information relating to ecological research. It provides scientists access to work related to ecological change.

NEDRES (NOAA Environmental Data Referral Service)

This site maintains a catalog of environmental data. It holds no actual data itself, but refers the user to the source containing the information.

CICNET

The CICNET gopher contains electronic journals in various subject categories, including the environment.

GLIN (Great Lake Information Network)

The user can find information on environmental quality, resource management and ecology of the Great Lakes region of the United States and Canada.

World Bank

Any large construction project funded by the World Bank includes a report on the environmental impact, if any, of the project. These reports are included in the Project Information Documents. A large number of these documents are maintained at this site.

United Nations

Various environmental reports and documents from the United Nations Conference on Environment and Development are available at this site.

2. Telnet

The "telnet" command allows the user to log in at remote sites. As a general rule, once connected, the user needs an account name and a password to log on. However, some sites are available to the public. Most of these sites either offer a menu with the account name and the password for public access areas of the site, or do not have account requirements at all, allowing the user free access to the site. There are other sites which allow access to the computer after the user has completed the registration process. After you have gained access to the site, you will usually be presented with a choice of the options available. The choices may include a listing of the different file areas available, the search options (by keyword, author, title etc.), the different BBSs which can be accessed, or a combination of all three. Unlike gopher, telnet connections can be used to download documents as well as software. The format of the command is:

telnet site-name

where site-name is the Internet address of the site you want to connect to. A list of site addresses and the information available is given in Table 2.

3. FTP

A number of FTP sites carry documents and data sets of interest to environmental professionals. However, since most of these sites are accessible via gopher, they will not be mentioned separately here. Some of the sites carry utility programs and documents that are of use to anyone using a computer.
These sites are:

wuarchive.wustl .edu
archie.au
nic.switch .ch
garbo.uwasa .fi

To access these sites via FTP, type 'ftp site-name' at the prompt, where "site name" is the name of the site that you want to connect to. When connected, you will be asked for a log in and a password. Send 'anonymous' as the log in, and your E-mail address as the password. This helps the network administrators keep track of how the system is being used.

Suggested Reading

A number of useful books and articles are available that describe the Internet, its function and the facilities available. Some of these books and articles are listed below.

1. *The Big Dummy's Guide to the Internet* by Adam Gaffin [*1*]. This book is widely available on the Internet. Contact the Electronic Frontier Foundation for a hard copy.
2. The column "Mining the Internet", by Judi Harris, in *The Computing Teacher* [*2,3*] These are a series of articles on how to use the Internet. For further information, see *The Computing Teacher* from Oct. 1992 to the present.
3. *Zen and the Art of the Internet*, by Brendan P. Kehoe [*4*]. This book is widely available on the Internet.

A number of other good books on the Internet are available on—line. If you do not yet have an Internet connection, look for "The Computing Teacher" or other literature on the Internet at your local library.

Concluding Remarks

The Internet is a useful part of a growing Information Superhighway It allows us to communicate, exchange data and to search for information. The information is scattered throughout the Internet. A compiled index of sites and the available information at these sites will be useful to those who use the Internet. It is hoped that more environmental organizations will establish Internet sites to share the vast amount of information available with them. We encourage you to use the Internet for your work.

Literature Cited

1. Gaffin, A., *The Big Dummy's Guide to the Internet*, Electronic Frontier Foundation (1993).
2. Harris, J., "Using the Internet Know-How to Plan How Students Will Know", *The Computing Teacher*, pp.35-40 (May 1993).
3. Harris, J., "Electronic "Packaging": File Types for File Transfers", *The Computing Teacher*, pp. 33-35(Oct.,1993).
4. Kehoe, B., "Zen and the Art of the Internet" (1992).
5. Gilster, P., "The Internet Navigator: A new users guide to network exploration", John Wiley and Sons, 496 pp., (1993).

Table 1. Public Access Internet Gateways

State/Province/City	Company	Number
ALBERTA		
Edmonton	PUCNet Computer Connections	(403)-484-5640 Voice help (4030 448-1901
CALIFORNIA		
Berkeley	Holonet	Free Trial (510) 704-1058 Voice help (510) 704-0160
Cupertino	Portal	(408) 725-0561 (408) 725-1724 (408) 973-8091 Voice help (408) 973-9111
Encinitas	Cyber Station	(619) 634-1376 Log on as 'guest'
San Diego Also provides local dial-in numbers for Los Angeles, Oakland and Irvine.	Dial N' CERF	Voice (619) 534-5087 or (800) 876-CERF
San Jose	Netcom	(510) 865-9004 (510) 426-6860 (408) 241-9760 (415) 424-0131
San Jose	A2i	(408) 293-9010 Log on as 'guest'
Sausalito	The Whole Earth 'Lectronic Link (WELL)	(415) 332-6106 Voice help (415) 332-4335
COLORADO		
Colorado Springs	CNS	(719) 570-1700 Voice help (719) 579-9120
Golden. Local dial-in numbers available in Ft. Collins, Denver, Boulder and Colorado Springs	Colorado Supernet	Voice help (303) 273-3471
ILLINOIS		
Chicago	MCSNet	(312) 248-0900 Voice help (312) 248-UNIX
Peoria	Peoria Free-Net	(309) 674-1100 Voice help (309) 677-2544
MARYLAND		
Baltimore	Express Access	(410) 220-0462 or (301) 220-0462 Voice help (301) 220-2020
MASSACHUSETTS		
Brookline	The World	(617) 739-9753 Voice help (617) 739-0202
Lynn	North Shore Access	(617) 593-5774 Voice help (617) 593-3110
Worcester	NovaLink	(508) 754-4009 Voice help (800) 274-2814
MICHIGAN		
Ann Arbor	MSEN	Voice help (313) 741-1120
Ann Arbor	Michnet	Voice help (313) 764-9430
NEW HAMPSHIRE	MV Communications, Inc.	Voice help (603) 429-2223
NEW YORK		
New York	Panix	(212) 787-3100 Voice help (212) 877-4854
New York	Echo	(212) 989-8411 Voice help (212) 255-3839
New York	MindVox	(212) 988-5030 Voice help (212) 988-5987

Table 1. ***Continued***

NORTH CAROLINA		
Charlotte	Vnet Internet Access	(704) 347-8839 Voice help (704) 374-0779
Triangle Research Park	Rock Concert Net	Voice help (919) 248-1999
OHIO		
Cleveland	Cleveland Free-Net	(216) 368-3888 Voice help (216) 368-8737
Cincinnati	Tri-State Free-Net	(513) 579-1990
Cleveland	Wariat	(216) 481-9436 (216) 481-9425 Voice help (216) 481-9428
Lorain	Lorain County Free-Net	(216) 277-2359 (216) 366-9753 Voice help (216) 481-9428
Medina	Medina Free-Net	(216) 723-6732 (216) 225-6732 (216) 335-6732
Youngstown	Youngstown Free-Net	(216) 742-3072
ONTARIO		
Toronto	UUNorth	Voice help (416) 225-8649
OREGON		
Beaverton	Techbook	(503) 220-0636 (503) 220-1016
Portland	Agora	(503) 293-1772 (503) 293-2059
PENNSYLVANIA		
Pittsburgh	Telerama	(412) 481-5302
QUEBEC		
Montreal	Communications Accessibles Montreal	(514) 281-5601 Voice help (514) 923-2102
RHODE ISLAND		
East Greenwich	IDS World Network	(401) 884-9002
VIRGINIA		
Norfolk	Wyvern Technologies	(804) 627-1828 (Norfolk) (804) 804-0662 (Peninsula)
WASHINGTON, D.C.	The Meta Network	Voice help (703) 243-6622
WASHINGTON STATE		
Seattle	Halcyon	(206) 382-6245 Voice help (206) 426 9298
Seattle	Eskimo North	(206) 367-3837 (206) 362-6731 Voice help (206) 367-7457

Table 2. Examples of sites available via teinet

SITE	BULLETIN BOARDS AVAILABLE	INFORMATION
ttnbbs.rtpnc.epa.gov	OAQPS - Office of Air Quality Planning and Standards. This BBS contains information on the services and activities of the OAQPS and its divisions, which are: 1. The Air Quality Management Division. 2. Emission Standards Division. 3. Technical Support Division, and 4. Stationary Source Compliance Division.	This is the major source of regulatory software and information in the United States. It contains software, standard methods and references, compliance information, policy guidelines, the latest regulations and data on air pollution. A 'must-see' site for air pollution professionals.
	AIRS - Aerometric Information Retrieval System. This site contains AIRS related software, and information on meetings, conferences, training seminars and permits.	
	AMTIC - Ambient Monitoring Technology Information Center. Contains information on ambient monitoring methods, quality assurance and quality control, and the promulgated regulations which have a bearing on ambient monitoring.	
	APTI - Air Pollution Training Institute. Training publications and activities,	

Table 2 Continued

	course curriculums, registration information, etc.	
	BLIS - BACT/ RACT/ LAER information. This site has a searchable database on the above topics. Also contains software and documents.	
	CAAA - Clean Air Act Amendments information. Contains summaries and full texts of Titles I through XI of the CAAA. Also, there are updates, policy/guidance memos, and recently signed rules.	
	CHIEF - ClearingHouse for Inventories and Emission Standards. Emission estimation software, emission inventory guidance and other emission factor & inventory information.	
	CTC - Control Technology Center. Software and files related to control technologies, list of ongoing projects, and more.	
	EMTIC - Emission Measurement Technical Information Center. EPA test methods, methods and regulations on a state-by-state basis, Federal Register publications,	

Table 2. Continued

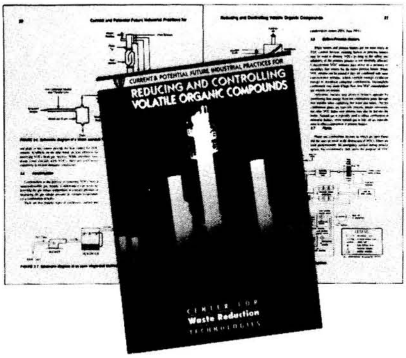
	Innovative technologies, and monitoring information.	
	NSR - New Source Review Technical and policy information on new sources.	
	SCRAM - Source Center for Regulatory Air Models. Regulatory models, meteorological data, model status, modeling guidance and tutorials on the available models.	
	NATICH - National Air Toxics Information Clearinghouse. Regulatory programs of the states, acceptable ambient guidelines, and emission inventory data	
	COMPLI - COMPLIance information. Contains databases on 1. Asbestos contractors 2. Clarifications and determination issued by the EPA concerning selected subparts of the Federal Register. 3. EPA certified woodstoves and woodstove manufacturers. Other information at this site includes policy guidance and monitoring strategies.	

Table 2. Continued

	OMS - Office of Mobile Sources. Fuel economy and certification of vehicles. Software related to pollution by mobile sources.	
	ORIA - Office of Radiation and Indoor Air. Documents and software relating to radiation. So far, no indoor air quality software is available on the BBS	
fedworld.gov	BOM - Bureau Of Mines. Abandoned minelands research, mines data, technical news and software listings.	
	CLU-IN - Superfund Data and Information. Documents, Superfund database and software.	
	PPIC-BBS - Pollution Prevention and Ozone information.	
	Gulfline - Gulf coast pollution information.	
	NOAA-ESDD - NOAA Earth System Data Directory.	
	Offshore-BBS - Offshore oil and gas data.	
	ATTIC - Alternative Treatment Technology Information Center. Special Interest Groups (SIGs) for bioremediation, software and	

Table 2. Continued

	databases on alternative treatment and on treatability.	
	DRIPSS - Drinking water Information Processing Support. State and Federal standards and other files concerning drinking water	
	PIN-BBS - Pesticide Information Network. Chemical database and Pesticide Monitoring Information database.	
	SWICH - Solid Waste Management. To subscribe, call 1-800-677-9424	
	NPS-BBS - Non Point Source program. Large number of documents on various topics, including the Non point Source Program. Also has a number of public domain utilities.	
	OEA-BBS - Office of Environmental Affairs.	
	ORDBBS - Office of Research and Development	
epaibm.rtpnc.epa.gov	MDC - Marine Database and files.	A searchable database of reports, documents and publications related to environmental engineering, Search can be by keyword, subject, title, author, year of publication, corporate source or report number. Accepts wildcard character in searches.


CURRENT & POTENTIAL FUTURE INDUSTRIAL PRACTICES FOR
REDUCING AND CONTROLLING
VOLATILE ORGANIC COMPOUNDS
CENTER FOR
Waste Reduction
TECHNOLOGIES

Adsorption of Selenium on Hydrous Alumina

Mriganka M. Ghosh and Chris D. Cox
Department of Civil Engineering, The University of Tennessee, Knoxville, TN
Jill R. Yuan-Pan
Former Graduate Student, University of Missouri, Columbia, MO

Adsorption of selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) on hydrous alumina (γ-Al_2O_3) was studied using batch equilibrium experiments. pH, the single most significant parameter, affected both speciations of selenium (Se) and of surface hydroxo groups on alumina that, in turn, determined the extent of adsorption of the oxyanions. Adsorption of both anions could be described satisfactorily by the Triple Layer Model (TLM). In the presence of SO_4^{2-}, Se(VI) adsorption decreased significantly. Fixed bed adsorbers of alumina with an empty bed contact time (EBCT) of 2 minutes or longer provided excellent removal of Se(IV) from dilute aqueous solutions in the pH range of 5 to 8 for a long period. Spent alumina beds were successfully regenerated with 0.25 percent NaOH solution followed by rinsing with deionized water and 0.05 M HCl. While two percent of alumina was lost per cycle on an average, the loss in adsorption capacity of regenerated alumina was insignificant.

INTRODUCTION

Effects of selenium (Se) on human health have not been clearly established. Though recognized as an essential nutrient in animal and human diets, selenium in high dosage can be toxic with undesirable physical manifestations (Brooks [*4*]). There is a very narrow range between deficient and toxic levels of Se in animals; a clear knowledge of the processes affecting Se distribution in the environment is essential (Jacobs [*25*]). The maximum contaminant level (MCL) of total Se in potable water in the United States is 10 μg/l. The toxic effects of Se are highly variable and depend on chemical species, type of organism, and duration of exposure (National Academy of Sciences [*30*]). The normal human dietary intake of Se is about 200 μg/day; selenium toxicity may manifest at dietary levels of 600 to 6,340 μg/day (National Academy of Sciences [*29*]). Aqueous Se can be acutely toxic at all levels of the aquatic food chain with possible bioaccumulation in lower organisms such as algae. Measured acute toxicity concentration, expressed as 96-hr LC_{50}, causing 50 percent death in test organisms after 96 hours of exposure, range from 340 to 42,000 μg/L for aquatic invertebrates and from 620 to 28,500 μg/L for fish (National Academy of Sciences [*30*]). Studies at the Kesterson National Wildlife refuge in the San Joaquin Valley of California showed Se accumulation in plants in high enough concentrations to cause deformities in grazing animals; apparently, return irrigation water from 42,000 acres of arable land caused the alarmingly high Se concentration in Kesterson reservoir (Deverel, *et al.*, [*11*]).

Usually groundwaters in areas of seleniferous bed rock contain high concentrations of Se; concentrations as high as 1.22 mg/l have been reported in wells in Arizona (USEPA [*38*]). High concentrations have also been found in California, Nebraska, Kansas, Oklahoma, Colorado, and South Dakota (American Water Works Association [*1*]). An analysis of violations of the federal drinking water standards for selenium, revealed that 75 percent of the violations occurred in communities with a population of 1,000 or less (USEPA [*38*]). Selenium is commonly used in the manufacture of photoelectric and solar cells, photocopiers, stainless steel and ceramic; release of Se to natural waters from these industries is conceivable.

Chemistry of Selenium

Selenic acid, H_2SeO_4, is a weak acid with pKs of -3 (Lange, [27]) and 1.66 (Baes and Mesmer [2]). Soluble selenate is the predominant species naturally occurring in plants with high Se content. Se(VI) is stable under alkaline oxidizing conditions. Acidic, reducing conditions may favor the formation of elemental selenium (Se^0) and selenides (Se^{2-}). Though the oxygenation of Se(IV) to Se(VI) occurs slowly at pH 6.5 or higher, alkaline, well-aerated surface waters mainly contain stable Se(VI). Selenious acid, H_2SeO_3, has pKs of 2.75 and 8.5 (Baes and Mesmer [2]). Dissolved selenite occurs mostly as the biselenite ion ($HSeO_3^-$) in the pH range of 3.9 to 8 (Shamberger [36]). Further, selenites are less soluble than selenates (National Academy of Sciences [30]).

The redox reactions in natural systems play a central role in the transport, availability, and toxicity of Se. Aqueous Se exists predominantly as selenates (+VI) and selenites (+IV). A significant amount of selenium in seleniferous soil is also found as soluble and insoluble inorganic compounds as a result of decomposition of plants with a high Se content. Most studies on Se in soils deal with selenite retention in acid soils (Se is immobilized as sesquioxides (Se_6O_4)) (Cary *et al.*, [7]). A ferric oxide-selenite sorption complex, that forms rapidly upon addition of selenite to soils, primarily governs Se concentration in soil solutions. It is also found associated with aluminum and soil organic matter (Levewque [28]). Chemically, Se is similar to sulfur, a group VI non-metal, which forms oxyacids of strengths similar to those of sulfur. High concentrations of sulfate can compete with selenite for surface sites (Brown and Carter [5]). Though pH is an important determinant for selenite sorption, in the presence of sulfate, its effect is minimal (Neal et al., [31]). Orthophosphate also competes favorably with selenite for sorption on soils; ligand exchange has been proposed as the mechanism of sorption for both of these oxyanions (Neal et al., [31, 32]). Selenite adsorption on hydrous oxides was found to be inversely related to pH (Hingston *et al.*, [20]; Yuan, [42]); the sorption maximum was insensitive to ionic strength indicating that the diffuse double layer may play only a minor role in the sorption process. While selenite desorption from goethite and gibbsite was extremely slow, selenate could be easily desorbed from these surfaces with NaCl solution at constant pH (Hingston *et al.*, [20]).

The literature on the sorption of selenate on hydrous oxides is sparse. Davis and Leckie [10] found essentially identical sorption of selenate and sulfate as a function of pH on amorphous iron oxyhydroxide. The adsorption of selenate on γ-alumina was reportedly much lower than that of selenite (Yuan, 1984; Balistrieri and Chao [3]), possibly because of different affinity of the two species for the hydrated oxide surface. Until recently, the mechanisms proposed for the adsorption of Se on hydrous oxides have almost entirely been based on equilibrium studies. Zhang and Sparks [43] have recently presented results on the kinetics of adsorption of Se on goethite based on pressure-jump relaxation methods. Selenite adsorption seemed to proceed in two steps: An outer-sphere complex is formed first, followed by the formation of an inner sphere complex as the adsorbed selenite replaces a H_2O from the protonated surface hydroxyl group. Two types of complexes, $\equiv SHSeO_3^0$ and $\equiv SSeO_3^-$, are formed. Selenate adsorption on goethite is nonspecific; it forms a single outer-sphere complex ($\equiv SOH_2^+—SeO_4^{2-}$) through electrostatic attraction accompanied by protonation; seemingly, two separate binuclear steps, protonation and adsorption, are involved.

Removal of Selenium

Selenium can be removed from dilute aqueous solutions by coagulation with hydrolyzing metals. Sorg and Logsdon [37] reported a Se(IV) removal of less than 20 percent by alum coagulation and between 50 to 70 percent removal by coagulation with ferric sulfate. A removal of less than 45 percent was obtained with lime-soda softening. Based on limited laboratory studies, removals in excess of 97 percent were obtained by both ion exchange and reverse osmosis. Recently, highly selective removal of Se(IV) on tailored chelating polymers, with immobilized Cu(II) present at the sorption sites, has been reported (Ramana and Sengupta [34]). Adsorption of ions on hydrous oxides, such as hydrated activated alumina or amorphous ferric oxides (as in coagulation), appears to be an inexpensive method for removing trace contaminants. Alumina behaves virtually as an amphoteric ion exchanger; oppositely charged functional groups (H^+, OH^-) may be adsorbed specifically on its surface. Though sometimes preceded by the formation of surface complexes, ultimately a ligand exchange reaction may lead to the removal of the oxyanions of Se. Alumina can be viewed as a weak-acid cation exchanger or a weak-base anion exchanger; adsorption of inorganic salts on alumina is due to hydrolytic adsorption associated with aluminum and hydrogen ion exchange. If alumina is treated with an acid, it will be charged to a hydroxyl-bearing cation capable of binding the anions of various salts as water-insoluble salts. Since activated alumina is an amphoteric substance, it will adsorb anions at pHs less than its isoelectric point. Therefore, the adsorption of an anion can be accomplished in a three step process:

1) Acidification: Alumina—HOH + HCl → Alumina—HCl + H_2O
2) Preferential adsorption: Alumina—HCl + X^- → Alumina—HX + Cl (provided the solubility of alumina-HX is less than that of alumina—HCl)
3) Regeneration: Alumina—HX + 2NaOH → Alumina—NaOH + NaX + H_2O

The regenerated alumina can be acidified and the adsorption process repeated: acidification: Alumina—NaOH + 2HCl → Alumina—HCl + NaOH + H_2O

The present paper deals with modeling of results of sorption of selenite and selenate on γ-Al_2O_3, obtained in batch equilibrium studies, using the triple-layer model (TLM) (Hayes and Leckie [16]). Results on the removal of these ions in column reactors of alumina, virgin and regenerated, are also presented. The objective of the study was to establish the removal capacities of commercial alumina for removing Se at different pHs and in the presence of other inorganic ions commonly found in natural waters such as sulfate. The effect of empty bed contact time (EBCT) and mass loading rate (MLR) on removal in fixed bed adsorbers was also investigated. Further, regeneration of spent alumina was studied to determine the reuseable capacity of sorbent and the loss of alumina during regeneration.

METHODS AND MATERIALS

Activated Alumina

All adsorption experiments were conducted using 92 percent pure γ-Al_2O_3 (Alcoa F-1 alumina); NaCl was used to maintain constant ionic strength of alumina suspension. The BET surface area of the 28×48 mesh alumina used was 250 m^2/g. The intrinsic acidity constants, pH_{zpc}, and surface site density, determined titrimetrically, were 6.0 (pK_{a1}^{int}), 10.2 (pK_{a2}^{int}), 8.1, and 2.4 sites/nm^2, respectively (Ghosh, 1986; Cox, 1992). The intrinsic acidity constants reported in Table 1 are for an ionic strength of 1×10^{-1} M (other TLM parameters are also listed in Table 1). The test alumina for any adsorption experiment was prepared by washing it with 0.01M NaOH followed by rinsing with deionized water until the pH and conductivity of the supernatant became constant. It was then dried at 105°C before use. All test solutions of Se were prepared using deionized (DI) water.

Table 1 Model Parameter Values for γ-Alumina Surface

Parameter		
$\log K_{a1}^{int}$	$\equiv SOH_2^+ \rightleftharpoons \equiv SOH + H^+$	−6.0
$\log K_{a2}^{int}$	$\equiv SOH \rightleftharpoons \equiv SO^- + H^+$	−10.2
$\log K_{Cl^-}^{int}$	$\equiv SOH + H^+ + Cl^- \rightleftharpoons \equiv SOH_2^+ - Cl^-$	7.58
$\log K_{Na^+}^{int}$	$\equiv SOH + Na^+ \rightleftharpoons \equiv SO^- - Na^+ + H^+$	−8.36
$\log K_{\equiv SOHSeO_3^2}^{int}$	$\equiv SOH + SeO_3^{2-} \rightleftharpoons \equiv SOHSeO_3^{2-}$	5.09
$\log K_{\equiv SOH_2^+ - HSeO_4^-}^{int}$	$\equiv SOH + SeO_4^{2-} + 2H^+ \rightleftharpoons \equiv SOH_2^+ — HSeO_4^-$	13.55
$\log K_{\equiv SOH_2^+ - SeO_4^2}^{int}$	$\equiv SOH + SeO_4^{2-} + H^+ \rightleftharpoons \equiv SOH_2^+ — SeO_4^{2-}$	10.13
$\log K_{\equiv SOH_2^+ - SO_4^{2-}}^{int}$	$\equiv SOH + SO_4^{2-} + H^+ \rightleftharpoons \equiv SOH_2^+ = SO_4^{2-}$	9.63
Surface Area	(m^2/g)	250
Site Density	$(sites/nm^2)$	2.4
C_1	(F/m^2)	1.4
C_2	(F/m^2)	0.2

Equilibrium Adsorption Experiments

All adsorption isotherms were obtained using the "bottle point" method. Predetermined amounts of washed alumina (1 to 5 g/l) were placed in 150 mL glass bottles. The ionic strength in all bottles was maintained at 10^{-1} M and the final sample volume was adjusted to 125 mL. The concentration of sorbate was varied from 0.006 to 0.600 mM. The pH was adjusted using 1 M NaOH or 1 M HCl. The bottles were continuously shaken for 48 hours at 20°C. Qualitative kinetic experiments, conducted over a one week period, indicated that adsorption continued at a very slow rate for an undetermined time period. After reviewing numerous data sets of ion adsorption on ferrihydroxides, (Dzombak [*12*]) an asymptotical approach to equilibrium was hypothesized. An arbitrary "equilibrium" time of 48 hours was chosen for adsorption experiments. In all cases, the quantity adsorbed after 48 hours was greater than 95 percent of the amount adsorbed in one week. After the bottles were removed from the shaker the pH was recorded and the contents passed through 0.45 μm Millipore filter. Selenium concentrations were determined using atomic absorption spectrophotometry (AAS) following hydride reduction. Se(VI) was reduced to Se(IV) by heating a 5 mL sample mixed with 3.5 mL of 36.5 percent HCl and 4.0 mL 25 percent NH_4Cl for thirty minutes in a water bath, prior to hydride reduction and AAS analysis.

Column Studies

In separate experiments, solutions of selenite (pH = 7.0; I = 0.025M) and selenate (pH = 4.0; I = 0.025M) were fed continuously to a glass column, 0.9 cm diameter, 76 cm long, containing F-1 Alcoa alumina supported by glass wool. The empty bed contact time (EBCT) was varied from 0.8 to 2.0 minutes by using different amounts of alumina in the sorption column. The feed solution was pumped from a 20 L Nalgene carboy at a constant rate maintained by a peristaltic pump attached to the effluent end; the hydraulic loading rate (HLR) ranged from 45 to 132 m^3/m^2-d in different experiments. A blank column containing no alumina was also run to determine the loss of selenium by adsorption on column wall and glass wool packing at the inlet and outlet ends of the column. Selenium loading on alumina was calculated from the total weight of Se *removed* per unit weight of alumina in the column. This was obtained from the difference in concentration between influent and total effluent volume collected during a given experiment. An experiment was terminated when either the adsorption capacity of alumina was exhausted or no breakthrough of Se occurred in 30 days.

To determine optimum conditions for regeneration, based on the loss of sorbent and regenerated sorption capacity, spent alumina beds were rinsed with NaOH solution of varying strengths, 0.25, 0.5, and 1 percent, applied in an upflow mode at a rate of 79.2 m^3/m^2-d. Rinsing the bed with 85 bed volumes (BV) of 0.25 percent NaOH solution followed by 5 BV of 0.05 M HCl and 4 BV of DI water yielded optimum results. The bed volume (BV), calculated as the product of column area, EBCT and HLR, was a variable in these experiments; it ranged from 2.5×10^{-3} to 6×10^{-3} L.

Modeling Selenium Adsorption

Recent investigations of Se adsorption by geothite (Hayes *et al.*, [*18*]; Zhang and Sparks, [*43*]) suggest that selenite and selenate adsorb to oxide surfaces by the formation of inner- and outer-sphere complexes, respectively. Inner- and outer-sphere complexes are possible in either the Stern or the triple-layer surface complexation models. In the present study, the latter, as interpreted by Hayes and Leckie [*16*], was used.

One difficulty in using the triple-layer model (TLM) is the large number of parameters that must be evaluated. For instance, to calculate the surface charge resulting from protonation, values of eight parameters must be known: four intrinsic equilibrium constants, two differential capacitances, the total site concentration, and the surface area. It is not possible to define a unique set of triple-layer parameters for a given data set because of interdependence among model parameters (Stumm *et al.*, [*39*]; Westall and Hohl [*40*]; Dzombak and Morel [*13*]). However, many parameters can be constrained

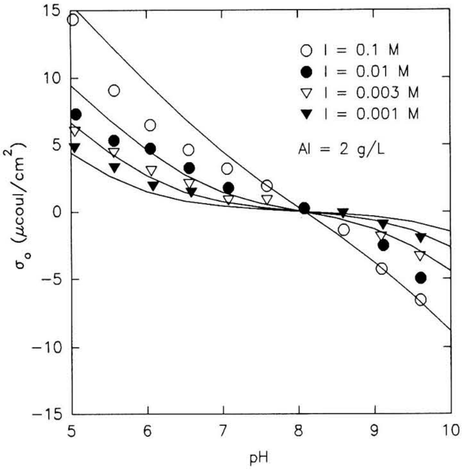


FIGURE 1. Distribution of surface charge on γ-Al_2O_3 (Solid lines represent model predictions).

Table 2 Triple-layer Surface Complexation Model for Selenite and Selenate Adsorption in the Presence of Sodium, Chloride and Sulfate Ions

I. Reactions and Equilibria

$\equiv SOH_2^+ \rightleftharpoons \equiv SOH + H^+$

$$K_{a1}^{int} = \frac{[\equiv SOH][H^+]}{[\equiv SOH_2^+]} \exp[-F\psi_0/RT] \qquad (3)$$

$\equiv SOH \rightleftharpoons \equiv SO^- + H^+$

$$K_{a2}^{int} = \frac{[\equiv SO^-][H^+]}{[\equiv SOH]} \exp[-F\psi_0/RT] \qquad (4)$$

$\equiv SOH + Cl^- + H^+ \rightleftharpoons \equiv SOH_2^+ - Cl^{-1}$

$$K_{Cl^-}^{int} = \frac{[\equiv SOH_2^+ - Cl^-]}{[\equiv SOH][Cl^-][H^+]} \exp[-F(\psi_\beta - \psi_0)/RT] \qquad (5)$$

$\equiv SOH + Na^+ \rightleftharpoons \equiv SO^- - Na^+ + H^+$

$$K_{Na^+}^{int} = \frac{[\equiv SO^- - Na^+][H^+]}{[\equiv SOH][Na^+]} \exp[-F(\psi_0 - \psi_\beta)/RT] \qquad (6)$$

$\equiv SOH + SeO_3^{2-} \rightleftharpoons \equiv SOHSeO_3^{2-}$

$$K^{int}_{\equiv SOHSeO_3^{2-}} = \frac{[\equiv SOHHSeO_3^{2-}]}{[\equiv SOH][SeO_3^{2-}]} \exp[-2F\psi_0/RT] \qquad (7)$$

$\equiv SOH + SeO_4^{2-} + 2H^+ \rightleftharpoons \equiv SOH_2^+ - HSeO_4^-$

$$K^{int}_{\equiv SOH_2^+ - HSeO_4^-} = \frac{[\equiv SOH_2^+ - HSeO_4]}{[\equiv SOH][SeO_4^{2-}][H^+]^2} \exp[-F(\psi_\beta - \psi_0)/RT] \qquad (8)$$

$\equiv SOH + SeO_4^{2-} + H^+ \rightleftharpoons \equiv SOH_2^+ - SeO_4^{2-}$

$$K^{int}_{\equiv SOH_2^+ - SeO_4^{2-}} = \frac{[\equiv SOH_2^+ - SeO_4^2]}{[\equiv SOH][SeO_4^2][H^+]} \exp[-F(2\psi_\beta - \psi_0)/RT] \qquad (9)$$

$\equiv SOH + SO_4^{2-} + H^+ \rightleftharpoons \equiv SOH_2^+ - SO_4^{2-}$

$$K^{int}_{\equiv SOH_2^+ - SO_4^{2-}} = \frac{[\equiv SOH_2^+ - SO_4^{2-}]}{[\equiv SOH][SO_4^{2-}][H^+]} \exp[-F(2\psi_\beta - \psi_0)/RT] \qquad (10)$$

II. Site Balance

$$\begin{aligned} S_T = {} & [\equiv SOH] + [\equiv SOH_2^+] + [\equiv SO^-] + [\equiv SOH_2^+ - Cl^-] \\ & + [\equiv SO^- - Na^+] + [\equiv SOHSeO_3^{2-}] + [\equiv SOH_2^{2+} - HSeO_4] \\ & + [SOH_2^+ - SeO_4^{2-}] + [\equiv SOH_2^+ - SO_4^{2-}] \qquad (11) \end{aligned}$$

III. Charge Balances

$$\begin{aligned} \sigma_0 = {} & [\equiv SOH_2^+] + [\equiv SOH_2^+ - Cl^-] + [\equiv SOH_2^+ - HSeO_4^-] + [\equiv SOH_2^+ - SeO_4^{2-}] \\ & + [\equiv SOH_2^+ - SO_4^{2-}] - [\equiv SO^-] - [\equiv SO^- - Na^+] - 2[\equiv SOHSeO_3^{2-}] \qquad (12) \end{aligned}$$

$$\sigma_\beta = -[\equiv SOH_2^+ - Cl^-] - [\equiv SOH_2^+ - HSeO_4^-] - 2[\equiv SOH_2^+ - SeO_4^{2-}] - 2[\equiv SOH_2^+ - SO_4^{2-}] + [\equiv SO^- - Na^+] \qquad (13)$$

$$\sigma_0 + \sigma_\beta + \sigma_d = 0 \qquad (14)$$

IV. Electric Double Layer Model

$$\psi_0 - \psi_\beta = \frac{\sigma_0}{C_1} \qquad (15)$$

$$\psi_\beta - \psi_d = -\frac{\sigma_d}{C_2} \qquad (16)$$

$$\sigma_d = -(8c\epsilon RT)^{1/2} \sinh\left(\frac{zF\psi_d}{2RT}\right) \qquad (17)$$

Notation: ψ = electrostatic potential, σ = charge density, c = electrolyte ion concentration, ϵ = permittivity of water, R = gas constant, T = absolute temperature, F = Faraday's constant, charge on electrolyte ion. Subscripts: o = surface plane, β = beta plane, d = diffuse layer plane by experimental data, while other parameters can be fixed by accepted conventions. Critical parameters can be identified by sensitivity analysis, and optimized by nonlinear least-squares regression of titration data.

FITEQL (Westall [*41*]), a nonlinear least-squares optimization program for estimating chemical equilibrium constants—including those of various surface complexation models (SCMs)—was used in model calibration. A BET surface area of alumina of 250 m^2/g, reported by the manufacturer, was used in the model. The outer layer capacitance (C_2) of the surface was set equal to 0.2 F/m^2 per standard convention. Assuming that the fixed surface charge is zero and that protons are the only ions adsorbing in the surface plane, the following relationship is valid:

$$PZC = \frac{pK_{a1}^{int} + pK_{a2}^{int}}{2} = \frac{\Delta pK_a^{int}}{2} \qquad (1)$$

The PZC and ΔpK_a^{int} were chosen as the model parameters in this study; thus only ΔpK_a^{int} needed to be determined to define K_{a1}^{int} and K_{a2}^{int}. The PZC of alumina, determined from the point of intersection of surface titration curves (Figure 1), was 8.1. The model was insensitive to ΔpK_a^{int} in that other model parameters, specifically pK_{an}^{int} and pK_{cat}^{int}, could compensate for changes in this parameter. So, a unique set of fitting parameters could not be defined and, consequently, the value of ΔpK_a^{int} could not be determined by fitting the model to titration data (Koopal et al., [*26*]; Cox and Ghosh [*9*]). Thus, the value had to be established independently. Such compensation among model parameters is well documented in the literature (Stumm *et al.*, [*39*]; Westall and Hohl [*40*]; Dzombek and Morel [*13*]; Koopal *et al.*, [*26*]; Hayes *et al.*, [*19*]). However, it should not be inferred that the surface speciation is irrelevant to adsorption of Se (or any other ion) in the TLM. For example, if the value of ΔpK_a^{int} is modified without compensation by changing other model parameters, a different prediction of Se adsorption would result. A γ-Al_2O_3 coated electrode was used to estimate a value of 4.2 for ΔpK_a^{int} of alumina (Bousse *et al.*, [*6*]). A surface site density of 2.4 site/nm^2 (Table 1) was used to calibrate the model.

The values of K_{an}^{int}, K_{cat}^{int}, and the inner-layer capacitance (C_1) were determined by calibration of the model using the results of titration of alumina suspension (2 g/L as Al; I = 0.1 M). The resulting model parameters are summarized in Table 1, and a comparison between measured and calculated values of surface charge as a function of pH are shown in Figure 1. The surface charge, σ_0 (coul/m^2), was calculated from titration data using the equation below:

$$\sigma_0 = (F/S)(C_A - C_B + [H^+] - [OH^-]) \qquad (2)$$

where F is Faraday's constant, S is the surface area of adsorbent per unit volume of suspension, and $C_A - C_B$ is the net concentration of acid or base added to the solution (M). It is assumed that neither electrolyte ion, Na^+ or Cl^-, adsorbs on the surface plane and that the fixed surface charge is zero.

In addition to the parameters necessary to describe titration data, equilibrium constants for the appropriate solution- and surface-complexation reactions are required to calculate the adsorption behavior of selenite and selenate. Speciation of aqueous Se was calculated from acidity constants for selenite ($pK_{a1} = 2.61$, $pK_{a2} = 8.46$) and selenate ($pK_{a2} = 1.7$). The pertinent surface reactions, equilibria, and the site and charge balance equations for the adsorption of selenite and selenate on alumina in the presence of NaCl as the background electrolyte are shown in Table 2; possible outer-sphere complexation by SO_4^{2-} and the appropriate equations for the electric double layer are also given. A schematic of the triple-layer model is given in Figure 2 showing the identity of relevant ions in appropriate layers. As shown in Figure 2, the only inner sphere complex considered in the TLM is $\equiv SOHSeO_3^{2-}$ (eq. 7, Table 2). All other ions form outer-sphere complexes on β plane (Figure 2). The surface complexation constants for Se were determined by fitting adsorption data to the model using FITEQL. Various adsorption reaction stoichiometries were considered; the minimum number of surface reactions yielding the best fit were selected. For selenate, two reactions were necessary to obtain good fit to the data as shown in Table 2.

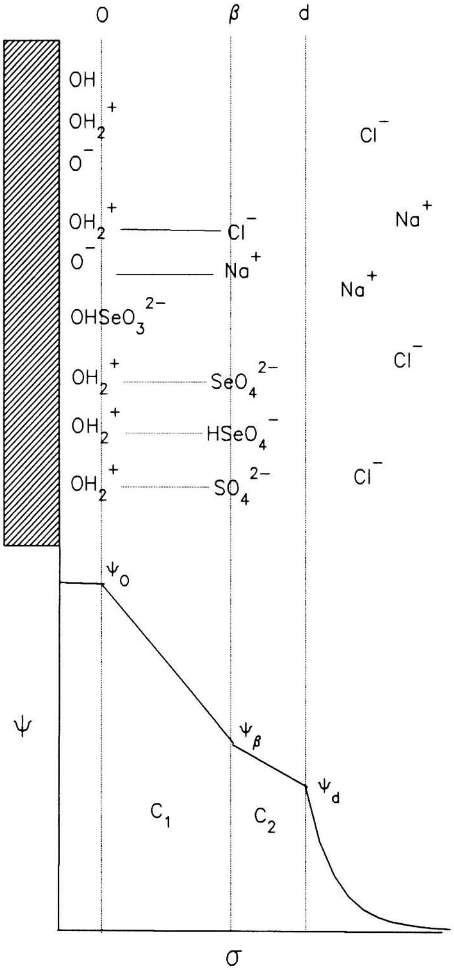


FIGURE 2. Schematic diagram of triple layer model.

RESULTS AND DISCUSSION

Equilibrium Adsorption

The effect of pH on the adsorption of selenite on alumina is shown in Figure 3. In these experiments the initial concentration of Se was varied from 0.0057 mM to 0.6 mM, while the alumina concentration (3.3 g/L as Al) was held constant. As expected, the adsorption pH-edge shifted to lower pH levels with an increase in sorbate-to-sorbent ratio. The removal was 100 percent at a pH of 5.5 or less for all initial concentrations of selenite tested (results not shown). At very low ratios, virtually all of Se(IV) was adsorbed, even at pHs higher than the PZC (8.1) of alumina. At all initial concentrations of Se(IV), the triple-layer model agreed very well with experimental data. Only one surface complex, an inner-sphere complex (eq. 7,

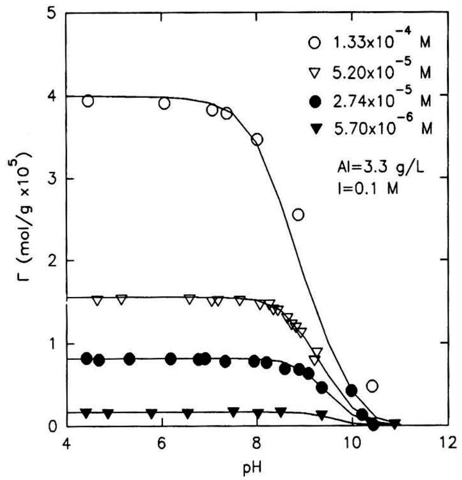


FIGURE 3. Adsorption of selenite as a function of pH (Solid lines indicate model predictions).

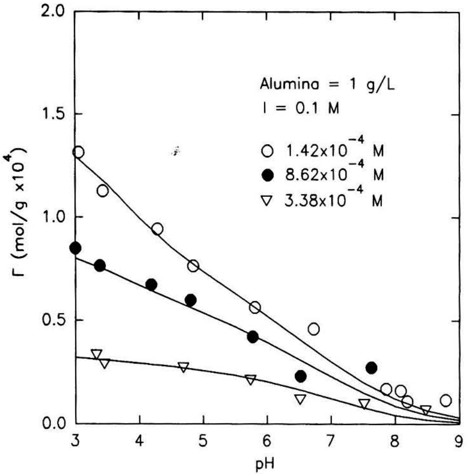


FIGURE 5. Adsorption of selenate as a function of pH (Solid lines indicate model predictions).

Table 2), with no ligand exchange, was needed to obtain such congruence. Novak *et al.*, [*35*] postulated chemisorption via hydrogen bonding to be largely responsible for Se(IV) sorption. However, at $pH > pH_{pzc}$, $HSeO_3^-$ is the only species capable of specific adsorption through hydrogen bonding (Hingston *et al.*, [*20*]). But, significant adsorption occurs at $pH > pK_{a2} > pH_{zpc}$ for Se(IV) suggesting that an alternate mechanism for adsorption of Se(IV) on negative surfaces must exist. Figure 4 shows a speciation of selenite in the adsorbing system; up to a pH of 7 most of the ion exists as a surface complex.

Figure 5 shows that the adsorption of Se(VI) was more strongly dependent on pH than that of Se(IV) for the range of initial concentration of adsorbate tested. For each sorbate to sorbent ratio, the adsorption density decreased with increasing pH over the entire range of pH studied; no adsorption pH-edge or adsorption maximum was discernible. The surface complexation constants to fit all data given in Figures 1-6 are given in Table 1. At a pH of 3 or less, adsorption was 100 percent for an initial selenate concentration (C_0) of 0.142 mM while that for $C_0 = 0.338$ mM was 85 percent. Novak *et al.*, [*33*] reported similar results for adsorption of Se(VI) on alumina, except that 100 percent adsorption of Se(VI) ($C_0 = 0.25$ mM) was obtained up to a pH of 7 (after which adsorption decreased sharply). Based on calorimetric measurements of heat of adsorption, the authors postulated ion exchange and electrostatic interactions to be the mechanisms of adsorption of Se(VI). However, no actual adsorption data were given by the authors, thus making a quantitative comparison difficult.

Although surface complexation models have successfully represented Se adsorption over the entire pH range (Davis and Leckie [*10*]; Dzombak [*12*], it must be realized that optimization of adjustable parameters in a mathematical model can produce good fit to experimental data, without confirming any mechanism of adsorption (Westall and Hohl, 1980). Table 3 compares the surface complexes that have been proposed by various researchers for the adsorption of selenite on oxide surfaces. Hayes *et al.*, [*18*], and Zhang and Sparks [*43*] have proposed inner-sphere surface complexes resulting from ligand exchange reactions. However, different sets of surface reactions were proposed, despite the fact that TLM was used to describe the adsorption of selenite on goethite in both studies. Though a ligand exchange reaction was invoked for the adsorption of selenite by hydrous ferric oxide (HFO) by Dzombak and Morel [*14*], an inner-sphere complex without ligand ex-

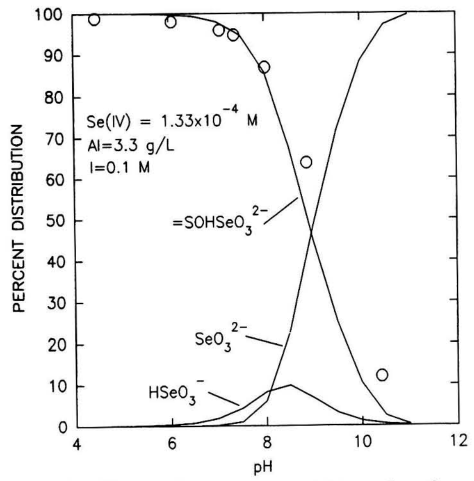


FIGURE 4. Distribution of selenium (IV) as a function of pH (Solid lines represent model predictions).

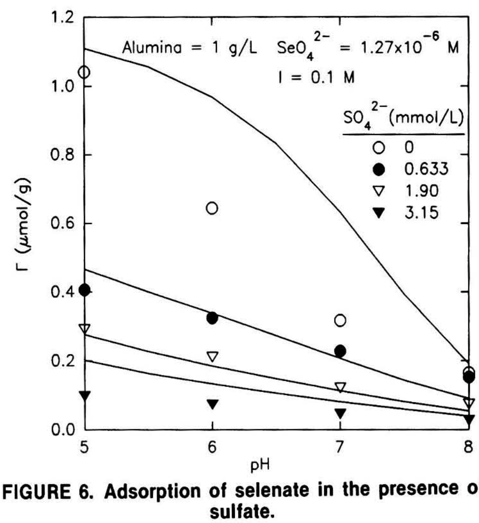


FIGURE 6. Adsorption of selenate in the presence of sulfate.

Table 3 Comparison of Surface Complexes of Selenite Used in Adsorption Models

Dzombak and Morel (1990), Hydrous Ferric Oxide, Generalized Two Layer Model	$\equiv SOH + SeO_3^{2-} + H^+ \rightleftharpoons \equiv SSeO_3^- + H_2O$	(18)
	$\equiv SOH + SeO_3^- \rightleftharpoons \equiv SOHSeO_3^{2-}$	(19)
Hayes et al. (1988), Goethite, Triple Layer Model	$\equiv SOH + SeO_3^{2-} + H^+ \rightleftharpoons \equiv SSeO_3^- + H_2O$	(20)
	$\equiv SOH + SeO_3^{2-} + H^+ + Na^+ \rightleftharpoons \equiv SSeO_3^- - Na^+ + H_2O$	(21)
Zhang and Sparks (1990), Goethite, Triple Layer Model	$\equiv SOH + SeO_3^{2-} + 2H^+ \rightleftharpoons \equiv SHSeO_3^0 + H_2O$	(22)
	$\equiv SOH + SeO_3^{2-} + H^+ \rightleftharpoons \equiv SSeO_3^- + H_2O$	(23)
This Study, γ-Al_2O_3, Triple Layer Model	$\equiv SOH + SeO_3^- \rightleftharpoons \equiv SOHSeO_3^{2-}$	(25)

change (eq. 19, Table 3), as used in this study, was also invoked. In each of these studies modeling is sensitive to available data. It is unlikely that the surface complexes required to fit a given set of data are the only reactions that occur on the surface. Each of the surface complexation reactions listed in Table 3 is reasonable and it is possible that all of these reactions are operative. However, a model may be sensitive to only one or two surface complexes for a given set of experimental conditions.

The surface complexes that have been proposed in recent years for the adsorption of selenate are compared in Table 4. With the exception of Dzombak and Morel [14], all researchers have proposed outer-sphere complexation of selenate. In Dzombak and Morel's generalized two-layer model only inner-sphere complexes are considered. However, outer-sphere complexation of selenate is clearly indicated by: 1) variation in adsorption behavior as a function of ionic strength (Hayes et al., 1988), 2) results of pressure jump experiments (Zhang and Sparks, 1990), and 3) in situ X-ray adsorption spectroscopy measurements (Hayes et al., 1987). Zhang and Sparks [43] used only one outer-sphere complex with a proton stoichiometry of unity, while an additional outer-sphere complex with a proton stoichiometry of two was included in the present study and by Hayes *et al.*, [18]. Inclusion of the two-proton surface complexation reaction resulted in a slightly better fit to the data, especially at low pH.

Table 4 Comparison of Surface Complexes of Selenate Used in Adsorption Models

Dzombak and Morel (1990), Hydrous Ferric Oxide, Generalized Two Layer Model	$\equiv SOH + SeO_4^{2-} + H^+ \rightleftharpoons \equiv SSeO_4^- + H_2O$	(23)
	$\equiv SOH + SeO_4^- \rightleftharpoons \equiv SOHSeO_4^{2-}$	(24)
Hayes et al. (1988), Goethite, Triple Layer Model	$\equiv SOH + SeO_4^{2-} + 2H^+ \rightleftharpoons \equiv SOH_2^+ - HSeO_4^-$	(25)
	$\equiv SOH + SeO_4^{2-} + H^+ \rightleftharpoons \equiv SOH_2^+ - SeO_4^{2-}$	(26)
Zhang and Sparks (1990), Goethite, Triple Layer Model	$\equiv SOH + SeO_4^{2-} + H^+ \rightleftharpoons \equiv SOH_2^+ - SeO_4^{2-}$	(27)
This Study, γ-Al_2O_3, Triple Layer Model	$\equiv SOH + SeO_4^{2-} + 2H^+ \rightleftharpoons \equiv SOH_2^+ - HSeO_4^-$	(28)
	$\equiv SOH + SeO_4^{2-} + H^+ \rightleftharpoons \equiv SOH_2^+ - SeO_4^{2-}$	(29)

Effect of Competitive Ions

The effect of several anions (SO_4^{2-}, HCO_3^-, and PO_4^{3-}) on the adsorption of oxyanions of Se on alumina was investigated to determine the feasibility of the process in natural water and industrial wastewater applications. Only the results of competition between selenate and sulfate are presented in Figure 6. The competitive effects of sulfate increases with decreasing pH. Sulfate is structurally similar to selenate. Therefore, not surprisingly, its adsorption behavior on alumina parallels that of Se(VI). Since sulfate is typically present in natural and most wastewaters at much higher concentrations than Se, its interference could potentially make removal of Se(VI) by activated alumina infeasible. Implication of sulfate interference for Se(IV) is less serious, as the process can be operated at a higher pH, where the affinity of sulfate for alumina is less. While TLM yielded satisfactory prediction of selenate adsorption in the presence of sulfate, the prediction with no sulfate added was unsatisfactory. No immediate explanation can be given for the observed low selenate sorption densities (Figure 6).

Adsorption in Fixed Beds of Alumina

Fixed bed adsorbers of Alcoa F-1 alumina were used to evaluate the effects of operational parameters, such as empty bed contact time (EBCT), hydraulic flow rate (HLR), and mass loading rate (MLR). The size and other characteristics of the adsorption columns were described earlier. For the purpose of comparison, a maximum contaminant level (MCL) of 10 $\mu g/L$ was taken as the upper boundary of column operation in

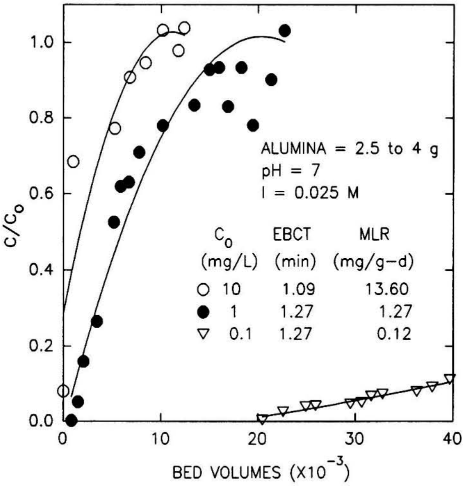


FIGURE 7. Removal of selenite in alumina columns at different mass loading rates.

Table 5 Removal of Selenite in Fixed Alumina Beds (pH = 7; I = 0.025M)

Column No.	C_0 (mg/L)	Wt of Alumina (g)	EBCT (min)	HLR (m/d)	MLR (mg/g-d)	Volume processed At MCL (m^3/m^2)	Volume processed At exhaustion (m^3/m^2)	Mass removed At MCL (mg/g)	Mass removed At exhaustion (mg/g)
1	10.0	3.7	1.09	79.3	13.6	0	600	0	29.35
2	1.0	3.0	0.81	80.2	1.7	14.8	1128	0.25	8.90
3	1.0	3.96	1.27	79.3	1.27	45.1	1329	0.73	7.60
4	1.0	4.5	1.54	79.2	1.12	88.5	1144	1.2	7.74
5	1.0	4.29	1.54	72.4	1.08	na	1286	na	8.04
6	1.0	4.15	1.54	70.11	1.07	na	1019	na	10.65
7	1.0	4.05	1.54	66.43	1.04	551.9	1193	8.32	14.09
8	0.1	2.46	1.27	45.27	0.12	1552	na	3.93	na

Note: Column 5 is 1× regenerated column 4
Column 6 is 2× regenerated column 4
Column 7 is 3× regenerated column 4

drinking water applications and bed exhaustion denotes a normalized effluent concentration (C/C_0) of 0.95.

The results of column experiments using different feed concentrations (C_0) of selenite (pH = 7.0; I = 0.025M) and different weights of alumina in the column are summarized in Table 5; columns 5, 6, and 7 were once, twice, and thrice regeneration of column 4. Regenerated alumina was used to determine any loss of sorption capacity that may result from reuse. Column 5, 6, and 7, operated till exhaustion, showed no decrease in adsorption capacity of regenerated alumina. The volume processed till exhaustion also compared well with that of virgin alumina (Column 2 and 3). Column 8, receiving 0.1 mg/L of Se(IV)—typically encountered in unpolluted natural waters—processed almost 1600 BVs till MCL was exceeded; the run was terminated after 30 days though the bed was still not exhausted. The effluent history profiles for selected column runs included in Table 5 are shown in Figure 7 to illustrate the effect of EBCT and MLR on removal. For a given C_0, EBCT and MLR are interrelated; removals are shown as a function of MLR. At an operational MLR of 0.12 mg/g-d, equivalent to $C_0 = 100$ μg/L operated at HLR = 79 m^3/m^2-d and an EBCT = 1.27 min, 20,000 bed volumes (BV) could be processed before breakthrough occurred. At these hydraulic rates, it is unrealistic to remove higher concentrations of Se(IV) in alumina adsorbers.

Table 6 summarizes the results of limited column studies on selenate removal at pH = 4.0 and I = 0.025M. To obtain different MLR, the HLR and C_0 were varied while the weight of alumina used in the adsorption column was kept constant (5.0 g). In dilute solutions, 100 μg/L or less as Se(VI), almost 4000 m^3 of water per m^2 (~38,000 BV) could be processed at an EBCT of only 1 minute before effluent concentration exceeded MCL (Column 1). By comparison, instantaneous breakthrough occurred in a column operated at an EBCT of 5 minutes while receiving selenate at a concentration of 1.0 mg/L at pH 7.0 (data not shown). However, the same column processed over 1550 BVs without any evidence of breakthrough when the influent was adjusted to pH 4. Clearly, alumina is not the adsorbent of choice if selenium is predominantly present as the hexavalent oxyanion. The low pH necessary for the satisfactory removal of Se(VI) may cause dissolution of alumina. The resulting concentration of aluminum in the treated water may be unacceptable from a public health standpoint. Representative effluent history profiles for the removal of selenate at pH 4 are shown in Figure 8. Sharp wavefronts shown in Figure 8 indicate excellent utilization of sorptive capacity of the columns.

The effect of sulfate on selenate removal in alumina adsorbers is shown in Figure 9. These results mimic what was observed in batch studies (Figure 6); significant competition between sulfate and selenate was exhibited at sulfate concentrations as low as 10 mg/L, even though the selenate MLR used (0.029 mg/g-d) was almost six-fold less than that (0.168 mg/g-d) used in Column 1 of Table 6, in the absence of sulfate. Only 20 BVs could be processed in the presence of 10 mg/l of sulfate before breakthrough occurred compared to 38,000 in the absence of sulfate.

Regeneration of Spent Alumina

Economics of adsorption processes are largely dependent upon the ability to regenerate spent beds. Sodium hydroxide was used to desorb Se from the alumina surface. Limited studies were conducted to determine the optimum concentration of NaOH that would produce good desorption without large loss of alumina; the regeneration experiments were limited to beds whose sorption capacities were exhausted while removing only selenite. As Table 7 indicates, the optimal restoration of sorptive capacity was obtained regenerating spent beds with 0.25 percent NaOH followed by rinsing with deionized water and 0.05 M HCl, in that order. Regenerated columns that were acid-rinsed demonstrated adsorption capacities equal to virgin alumina (Figure 10); in fact, up to about 6000 bed volumes, removal of Se(IV) was somewhat better than that with virgin alumina. After 2 or 3 regenerations, adsorption capacity improved somewhat in that the adsorption waves were not as sharp as with virgin alumina, though the exhaustion

Table 6 Removal of Selenate in Fixed Alumina Beds (pH = 4; I = 0.025M)

Column No.	C_0 (mg/L)	Wt of Alumina (g)	EBCT (min)	HLR (m/d)	MLR (mg/g-d)	Volume processed At MCL (m^3/m^2)	Volume processed At exhaustion (m^3/m^2)	Mass removed At MCL (mg/g)	Mass removed At exhaustion (mg/g)
1	0.1	5.0	1.0	132.4	0.168	3961	na	5	na
2	1.0	5.0	2.0	59.8	0.792	880	1390	11.92	13.67
3	5.0	5.0	2.0	65.5	4.18	0	519	0	15.54

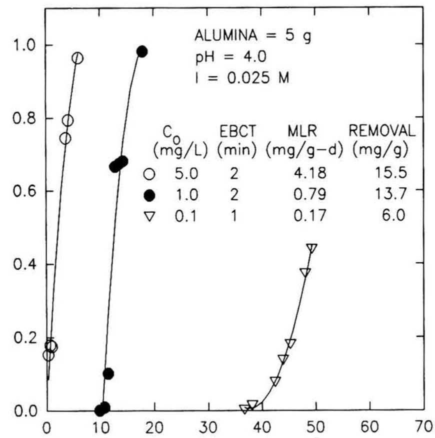


FIGURE 8. Removal of selenate in alumina columns at various mass loading rates.

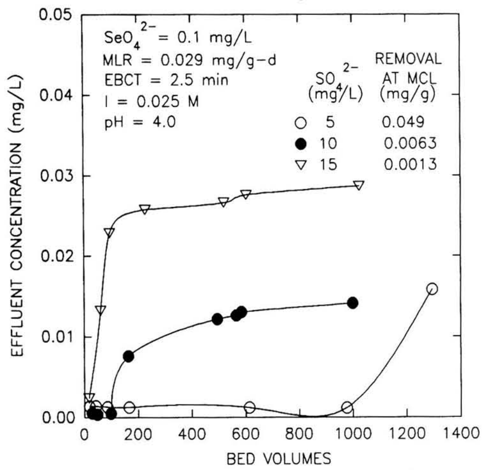


FIGURE 9. Effect of sulfate on removal of selenate in alumina columns.

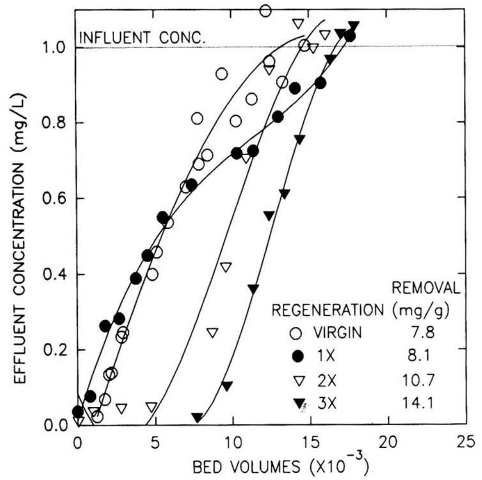


FIGURE 10. Removal of selenite by regenerated alumina.

Table 7 Regeneration of spent alumina

Column Number	Regenerant	Rate (m/d)	Number of Bed Volumes Applied	Adsorbate Recovered (%)	Alumina Lost (wt. %)
1	1% NaOH	79.2	75	85	11
2	0.5% NaOH	79.2	70	94	5
3	0.25% NaOH	79.2	70	84	4
4	0.25% NaOH	79.2	85		
	DI Water	79.2	4	94	2
	0.05 M HCl	79.2	5		

Bed Volume (BV) = $4.4 \times 10^{-5} \times$ duration $\times$ HLR $\times$ area of column where BV is in L, duration in min, and HLR in m/d

occurred at about the same time—16,000 bed volumes. No satisfactory explanation can be given to account for the observed increase in sorption capacity following regeneration.

SUMMARY AND CONCLUSIONS

Adsorption of Se on activated alumina is greatly affected by pH and competition with certain anions. High adsorption densities of Se(IV) and Se(VI) can be obtained at pH less than the pH_{pzc} of alumina. The adsorption of both oxyanions of Se could be described satisfactorily by the triple-layer model. Though effective adsorption of selenite occurred at pH 7 or less, adsorption of selenate decreased sharply above pH 4. If selenium occurs predominantly as selenate, adsorption on alumina may not be the method of choice for its removal. Dissolution of alumina at low pHs may cause aluminum concentration to rise to unacceptable levels in the treated water. Significant decrease in selenate removal occurred in the presence of small concentrations of sulfate. Competitive effects of interfering ions may be minimized by proper selection of the operating pH. However, the relative abundance of SO_4^{2-} in most natural waters and wastewaters may preclude the use of alumina for removing the hexavalent oxyanion of Se. Experiments with fixed beds of alumina indicated that both Se(IV) and Se(VI) can be effectively removed for long periods of time using an empty bed contact time of only 2 minutes, provided the equilibrium is favorable for selective adsorption of the oxyanions of the element. For designing such systems an EBCT of 5 min appears to be sufficient. Successful regeneration of spent alumina beds is feasible with 0.25 percent NaOH, followed by rinsing with water and dilute HCl to protonate the alumina surface. The loss of alumina can be held to less that 2 percent per cycle.

ACKNOWLEDGMENTS

This study was funded by a research grant from the Office of Exploratory Research and Development, U.S. EPA, Grant No. R8094 25010. Mention of trade names does not constitute endorsement either by the authors or EPA.

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Content and Fractionation of Heavy Metals in Soils of Two Contaminated Sites in Taiwan

G. Y. Shu and J. C. Liu

Department of Chemical Engineering, National Taiwan Institute of Technology,
Taipei, Taiwan

The rice paddies near Taoyuan County, Taiwan, were contaminated with trace metals by the effluent from two plasticizer plants in the seventies. A study was conducted to: (i) determine the total metal contents, (ii) compare the extraction strength of different solutions, and (iii) investigate the metal speciation. Total soil metals at site 1 ranged from: lead = 201 to 1955 mg Kg^{-1}*; cadmium = 18 to 205 mg* Kg^{-1}*; and zinc = 131 to 282 mg* Kg^{-1}*. Total soil metals at site 2 ranged from: lead = 80 to 148 mg* Kg^{-1}*; cadmium = 8 to 82 mg* Kg^{-1}*; and zinc = 55 to 65 mg* Kg^{-1}*. Five different extractants (4 N* HNO_3*, aqua regia, 0.1 N HCl, 0.002 M EDTA, and 0.002 M NTA) were utilized and compared. Sequential extraction was conducted to assess the metal speciation in soil systems. Lead was found to be predominantly organic-bound or oxide-bound. The exchangeable fraction was the dominant form of cadmium in both sites. Zinc was mostly oxide-bound. The potential impacts on groundwater quality by cadmium were assessed.*

INTRODUCTION

The two heavy metal contaminated sites are located in a rural agricultural area of northern Taiwan in Taoyuan County, as shown in Figures 1 and 2. Site 1 (17 hectares) formerly housed a chemical plant manufacturing plastic stabilizers, such as cadmium stearate and lead stearate. From 1973 to 1984, the chemical plant discharged wastewater containing heavy metals into an irrigation ditch which caused serious heavy metal pollution of rice, soil, and groundwater. The chemical plant was shut down by the government in 1984 due to violations of environmental regulations. In response to residents' demand, the Taiwan Environmental Protection Agency has begun a remedial investigation, focusing on the extent of contamination and technical alternatives of land reclamation.

Site 2 is about 30 km north of site 1. There is a chemical plant with the same manufacturing processes which has been operating since 1978. This plant has also caused serious heavy

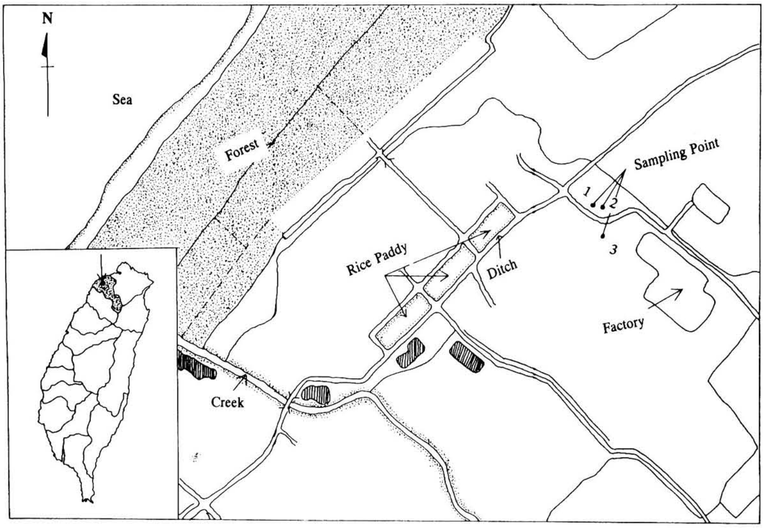

FIGURE 1. Map of contaminated site 1 located in the Vicinity of Taoyuan, Taiwan.

Correspondence concerning this paper should be addressed to J. C. Liu.

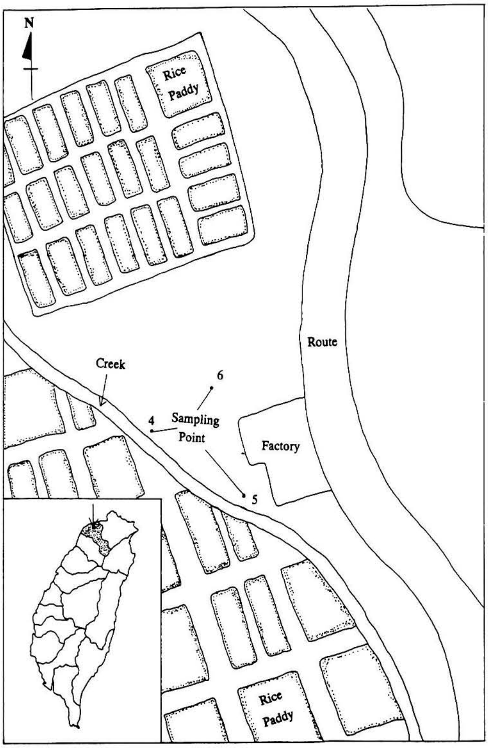

FIGURE 2. Map of contaminated site 2 located in the vicinity of Taoyuan, Taiwan.

metal pollution in an area of about 23 hectares. Considering that most other local residents rely on groundwater as their sole water supply, it is important to assess the transport of heavy metals in the soil systems. In this study, the basic physical-chemical properties of the soils were determined; different extractants were used to analyze total metal contents. Sequential extraction procedures were carried out to explore the metal speciation in the soil systems and to estimate the potential impacts on groundwater quality.

METHODS AND MATERIALS

Soil samples were collected to the depth of 30 cm. Three soil samples were taken for each site (Figures 1 and 2). Soils were air-dried, ground, and sieved by 20 mesh microsieves. Soil pH was determined from the soil solution (McLean [*12*]); and soil total organic carbon was determined by the TOC analyzer (I. O. Analytical, Model 700). The cation exchange capacity was determined from the saturated soil solution (Rhoades, [*14*]). Surface area was determined by the BET specific area analyzer (Micromeritics ASAP 2000). The basic properties of soils at site 1 and site 2 are shown in Table 1. Five different methods were used to analyze the total metal contents. In the first method, five grams of soil were put into a 250 ml pyrex flask, 10 ml of 4 HNO_3 were added to the soil, and the solution was mildly boiled on a hot plate. Nitric acid was intermittently added to prevent total dry-out until the supernatant became clear and apparent. Soil samples were then filtered through 0.45 μm filter papers (Gelman). Distilled water was added to the supernatant to a final volume of 100 ml. The metal concentrations were then measured by atomic absorption spectrophotometry (Varian Spectr AA-20). In the second method, aqua regia was used instead of nitric acid. The soil solution was covered by glass and heated without boiling until the soil solution became clear and apparent. Soil samples were filtered through 0.45 μm filter papers (Gelman). Distilled water was added to the supernatant to a final volume of 100 ml. The metal concentration was detected by atomic absorption spectroscopy. In the third method, 5 g of soil were placed in a 125 ml plastic bottle, 50 ml of 0.1 N HCl were added, shaken for 1 hr, run through filter papers (Whatman 42), and detected by atomic absorption spectroscopy. Chelating agents (EDTA and NTA) were used in the fourth and fifth methods. Five grams of soil and 50 ml of 0.002 M of EDTA or NTA were placed in a 125 ml plastic bottle, pH values were kept at 6.1 and 6.2, respectively, shaken for 12 hrs, run through filter papers (Whatman 42), and then detected by atomic absorption spectroscopy. In order to investigate the effect of pH values on the extraction of metals from soils with EDTA, experiments were conducted for pH nominally in the range of 3 to 11, and

Table 1 Basic Properties of Soils

	Site 1			Site 2		
Soil	1	2	3	4	5	6
pH	6.38	6.60	6.05	5.78	5.30	6.22
Sand (%)	54.5	54.5	54.5	0.1	0.1	0.1
Silt (%)	38.2	38.2	38.2	51.4	51.4	51.4
Clay (%)	7.3	7.3	7.3	48.3	48.3	48.3
CEC (meq/100g)	2.98	2.92	3.01	2.50	2.53	2.59
TOC (%)	0.91	1.91	0.73	0.72	0.74	0.39
BET Area (m^2/g)	16.64	12.17	24.56	2.64	2.47	3.60

Table 2 Sequential Extraction Procedures

Fraction	Extraction	Extraction Condition
Exchangeable	10 ml 1M $MgCl_2$	Shaken 1 hr at pH = 7
Carbonates-Bound	10 ml 1M NaOAc	Shaken 5 hr at pH = 5
Fe-Mn Oxides-Bound	20 ml 0.04 M $NH_2OH.HCL$	Shaken 5 hr at 85°C
Organic-Bound	20 ml 30% H_2O_2 and 10 ml conc. H_2SO_4	Shaken 2 hr and 3 hr, respectively, at 85°C
Residual	20 ml conc. H_2SO_4	Mildly boiled for 1 hr

Table 3 Extracted Lead Concentration (mg/Kg soil)

	1	2	3	4	5	6
4N HNO_3	1955.0	201.0	790.6	118.6	148.3	80.6
0.1 N HCl	1258.0	73.3	437.4	69.0	93.2	31.3
Aqua Regia	1600.0	189.0	527.2	126.2	156.6	67.6
0.002 M EDTA	1312.0	113.6	439.5	75.9	109.1	34.6
0.002 M NTA	998.3	93.4	347.4	55.3	75.1	20.5
Sequential Extraction	1909.5	257.5	763.0	166.5	298.5	104.5

Table 4 Extracted Cadmium Concentration (mg/Kg soil)

	1	2	3	4	5	6
4N HNO_3	205.0	18.1	25.0	82.3	80.6	8.2
0.1 N HCl	157.9	13.8	18.2	75.8	72.4	6.4
Aqua Regia	150.0	15.0	18.3	62.5	76.1	6.9
0.002 M EDTA	126.8	12.6	13.0	25.3	36.0	5.6
0.002 M NTA	121.3	11.0	10.7	19.6	26.8	5.0
Sequential Extraction	281.9	45.6	52.2	119.7	115.9	15.8

Table 5 Extracted Zinc Concentration (mg/Kg soil)

	1	2	3	4	5	6
4N HNO_3	282.0	114.6	131.0	65.3	55.6	58.3
0.1 N HCl	67.5	19.7	21.3	7.5	7.7	5.1
Aqua Regia	165.0	87.6	85.0	47.4	46.8	50.6
0.002 M EDTA	42.9	12.7	13.5	3.9	5.0	3.1
0.002 M EDTA	40.4	11.1	10.9	3.5	4.6	2.7
Sequential Extraction	283.8	125.1	141.8	79.2	82.0	85.0

were compared to water with constant ionic strength. In the metal speciation experiment, sequential extraction (Tessier *et al.*, [*20*]) procedures were utilized. The procedures are shown in Table 2.

RESULTS AND DISCUSSIONS

Results of total metal contents with 4 N HNO_3 are shown in and Tables 3 to 5. Soil at site 1 contains various concentrations of lead (201-1955 mg/Kg), cadmium (18-205 mg/Kg), and zinc (131-282 mg/Kg). Soil at site 2 contains lead (80-148 mg/Kg), cadmium (8-82 mg/Kg), and zinc (55-65 mg/Kg). These concentrations were higher than the background concentrations of typical soils in Taiwan and exceeded the maximum allowable concentrations (lead > 120 mg/Kg, cadmium > 10 mg/Kg, zinc > 80 mg/Kg).

Various extractants have been used to analyze the total metal concentration and the availability of metals, such as: aqua regia, concentrated nitric acid, diethylenetriamine-pentacetic acid (DTPA), ethylenediamine-tetraacetic acid (EDTA), calcium chloride, and sodium nitrate (Lindsay and Norvell [*10*]; Sauerbeck and Styperek [*16*]; Chen *et al.*, [*2*]). In this study, five different methods to analyze total metal contents were compared in order to get a better understanding of metal extraction from soils. In lead analysis, 4 N HNO_3 and aqua regia have stronger extraction capability than 0.1 N HCl, 0.002 M EDTA, and 0.002 M nitrilotriacetate (NTA). There is no significant difference in terms of the extraction capability for the latter three. In cadmium analysis, 4 N HNO_3 shows better extraction than the other four reagents. A different sequence was found for zinc analysis in which 4 N HNO_3, again, shows the best extraction. Generally speaking, the sequences can be written as:

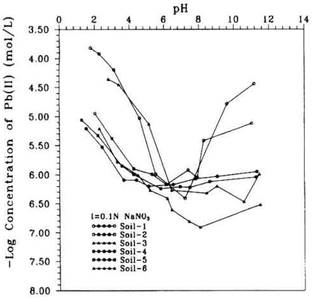

FIGURE 3A. Effect of pH values on the extracted Pb(II) concentration. Experimental conditions: 10 g/L solid, 0.1 N $NaNO_3$.

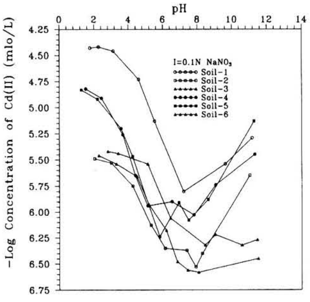

FIGURE 3B. Effect of pH values on the extracted Cd(II) concentration. Experimental conditions: 10 g/L solid, 0.1 N $NaNO_3$.

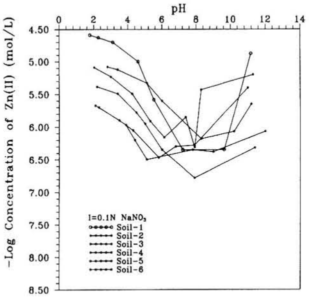

FIGURE 3C. Effect of pH values on the extracted Zn(II) concentration. Experimental conditions: 10 g/L solid, 0.1 N $NaNO_3$.

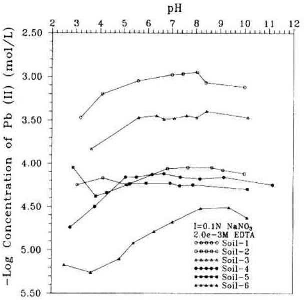

FIGURE 4A. Effect of pH values on the extracted Pb(II) concentration. Experimental conditions: 10 g/L solid, 0.1 N NaNO$_3$, 0.002 M EDTA.

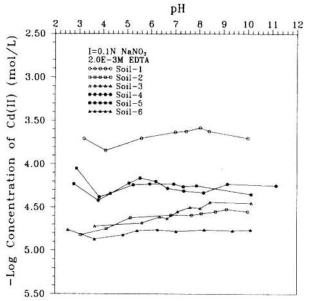

FIGURE 4B. Effect of pH values on the extracted Cd(II) concentration. Experimental conditions: 10 g/L solid, 0.1 N NaNO$_3$, 0.002 M EDTA.

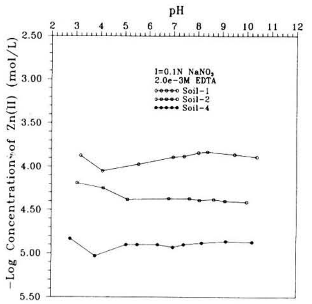

FIGURE 4C. Effect of pH values on the extracted Zn(II) concentration. Experimental conditions: 10 g/L solid, 0.1 N NaNO$_3$, 0.002 M EDTA.

Pb: 4N HNO$_3$, Aqua regia > 0.002 M EDTA > 0.1 N HCl, 0.002 M NTA

Cd: 4N HNO$_3$ > Aqua regia, > 0.1 N HCl > 0.002 M EDTA, 0.002 M NTA

Zn: 4N HNO$_3$ > Aqua regia > 0.1 N HCl > 0.002 M EDTA >0.002 M NTA

The effect of pH values on the extraction of metals from soils was examined. Results are shown in Figures 3A to 3C and 4A to 4C. It was obvious that the extracted metal concentrations varied with pH values when the extractant contained only simple salt, such as 0.1 N NaNO$_3$. Generally, metal concentrations in the solution phase decreased as pH values increased until pH reached neutral to slightly alkaline range, and then increased with pH values. However, the amount of metals extracted with 0.002 M EDTA did not exhibit a significant pH dependency. This was in accordance with previous research (Peters and Shem [*13*]).

With regard to soil systems, it has been indicated that metal speciation is closely related to bioavailability, toxicity, and mobility (Gunn *et al.* [*7*]). The metal availability either correlates best with free metal ion activity in the soil water (Bingham *et al.* [*1*]) or with organic complexes (Sposito [*19*]). Tessier *et al.* [*20*] found that the uptake was better correlated with easily-extracted fractions of metals. Since the relative impact of metals on the soil systems will be controlled by the major forms of metals that are present, the distribution of three heavy metals were explored. Results are shown in Figures 5A to 5F. It was postulated that the speciation of lead in contaminated soils was predominantly associated with Fe and Mn oxides (Levy *et al.* [*9*]). (Lion *et al.* [*11*]) found that lead and cadmium were mostly bound to Fe and Mn oxides and organic matters. Results in this study showed that the speciation of lead in site 1 was markedly different from that in site 2. The dominant form of lead in soils at site was organically bound, while oxide-bound lead was the dominant form at site 2. This could be correlated to the organic content of soils at site 1 and 2. Since the organic carbon of site 1 is generally higher than that of site 2, organic-bound lead in site 1 constitutes a higher percentage than in site 2. Cadmium in soil systems at site 1 and site 2 showed different characteristics. Though it has been pointed out that the cadmium was predominantly associated with Fe and Mn oxides in contaminated soils (Levy *et al.* [*9*]), exchangeable fraction was the dominant form of cadmium in both site 1 (Avg. 57.5 percent) and site 2 (Avg. 45.6 percent). Oxides-bound fraction of cadmium ranged from 9 percent to 36.5 percent. Zinc in both site 1 and site 2 are dominantly oxide-bound. The strong adsorption and coprecipitation of heavy metals have been pointed out in numerous studies (Schindler and Stumm, [*17*]; Fu and Allen [*5*]).

Concerning the mobility of heavy metals in the soil systems, Salomons [15]) studied river sediments and constructed the relationship between predicted dissolved copper concentration with the amount of exchangeable copper. Elliot *et al.* [*4*] pointed

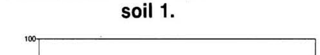

FIGURE 5A. Metal speciation of soil 1.

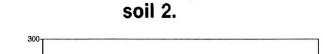

FIGURE 5B. Metal speciation of soil 2.

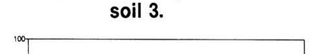

FIGURE 5C. Metal speciation of soil 3.

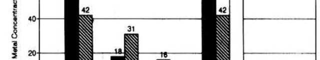

FIGURE 5D. Metal speciation of soil 4.

FIGURE 5E. Metal speciation of soil 5.

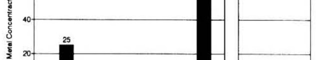

FIGURE 5F. Metal speciation of soil 6.

out that the non-detrital metals, such as the exchangeable, water soluble, and those adsorbed onto solid phase, would represent the most readily mobilized in soil-water systems under acidic conditions. Therefore, the potentially more mobile fraction consists of the exchangeable and the carbonate-bound. Lead ranges from 18.9 percent to 43.5 percent with the average at 13.4 percent. However, the average is 20 percent for soils from site 2. Though caution is required in interpreting the fractionation results (Shuman [*18*]; Kheboian and Bauer [*8*]; Clevenger [*3*]), it could be stated that lead at site 2 was potentially more soluble than lead at site 1. Summing the exchangeable and the carbonate-bound fractions together, the most soluable part of cadmium is 70.2 percent for site 1 and 66.4 percent for site 2. Zinc is relatively less mobile than lead and cadmium. On the basis of the relative amounts of each element released in the first two extraction steps, Cd would have the greatest mobility among the three metals in the soil-water systems. This is not unique, as cadmium has been found to be most easily released in contaminated soils (Gibson and Farmer [*6*]), and in water treatment sludges (Elliot *et al.*, [*4*]). The potential impacts on groundwater can be assessed by extrapolating data into field situations. Take the average precipitation of 200 $cmyr^{-1}$, and net infiltration as 100 $cmyr^{-1}$. Assuming the soil contains 126.7 $mgKg^{-1}$ of cadmium and 70.2 percent can be solubilized in site 1 within the first year, the cadmium concentration in the leachate would be 37.1 mgL^{-1}. This level is much higher than the drinking water standard of 0.01 mgL^{-1}. Similar calculation yielded cadmium concentration in the leachate from site 2 be 23.2 mgL^{-1}. Therefore, the groundwater in the vicinity of contaminated sites could be threatened by cadmium pollution.

SUMMARIES

The experimental results showed that: (1) The metal pollution in these two sites are very serious. The concentrations of lead, cadmium, and zinc all exceeded background levels. Among the five different extractants used, sequences of the strength of extraction varied when applied to different metals. Generally speaking, concentrated nitric acid and aqua regia are the best extractants. (2) Depending on the basic soil properties and metal types, dominant metal forms were different. Lead was mostly organic-bound in site 1, while oxide-bound in site 2. Exchangeable fraction was the dominant form of cadmium both in site 1 and site 2. Zinc in site 1 and site 2 were dominantly oxide-bound. (3) Supposing exchangeable and carbonate-bound fractions stand for the water-soluble part, cadmium was potentially the most easily released metal in these two sites. If soil were to become acidic ($pH > 5$), roughly 70.2 percent and 66.4 percent of cadmium in site 1 and site 2, respectively, could be solubilized. With approximately 100 $cmyr^{-1}$ net infiltration, an estimated 37.1 mgL^{-1} and 23.3 mgL^{-1} of cadmium would be found in leachates in site 1 and site 2, respectively. This calls for prompt response and sound management from the government.

ACKNOWLEDGMENT

The authors wish to acknowledge the support from the National Science Council, Taiwan, under Grant No. NSC-82-0421-E-011-037-Z.

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Biological Vapor-Phase Treatment Using Biofilter and Biotrickling Filter Reactors: Practical Operating Regimes

A. Paul Togna and Manjari Singh

Envirogen, Inc., Princeton Research Center, 4100 Quakerbridge Road,
Lawrenceville, New Jersey 08648

The biological treatment of volatile organic compounds (VOCs) and air toxics has received increased attention in recent years. Biotreatment of air-borne contaminants offers an inexpensive alternative to conventional air treatment technologies such as carbon adsorption and incineration. Most biological air treatment technologies commercially available are fixed-film systems that rely on growth of a biofilm layer on an inert organic support such as compost or peat (biofilters), or an inorganic support such as ceramic or plastic (biotrickling filters). If designed properly, these systems combine the advantages of high biomass concentration with high specific surface area for mass transfer.

At economically viable vapor residence times (1 to 1.5 minutes), biofilters can be used for treating vapor streams containing up to approximately 1500 μg/L of readily biodegradable compounds. Biotrickling filters may offer greater performance than biofilters at high contaminant loadings, possibly due to higher internal biomass concentrations. Both systems are best suited for treating vapor streams containing one or two major compounds. If designed properly, biofilters are especially well suited for treating streams that vary in concentration from minute to minute.

INTRODUCTION

The biological treatment of VOCs and air toxics has received increased attention in recent years. Biotreatment of air-borne contaminants offers an inexpensive alternative to conventional air treatment technologies such as carbon adsorption, wet scrubbing, and incineration.

Vapor-phase problems can be roughly separated based on contaminant concentration, stream composition, and vapor flow rate. The bioreactor configuration best suited for one particular application may not be suitable for others. For example, low flow rate vapor streams are most efficiently treated biologically within a bubble column, stirred tank, or airlift loop configuration, where the vapor stream of interest is bubbled into a vessel containing a suspended culture of microorganisms. Alternative bioreactor designs which have much lower pressure drops must be used at higher air flow rates (typically greater than 5000 scfm) to compete favorably with conventional technologies. Most of these high flow rate biological air treatment designs which are commercially available are fixed-film systems that rely on the growth of a biofilm layer on an inert organic support such as compost or peat (biofilters), or an inorganic solid support such as ceramic or plastic (biotrickling filters). If designed properly, these systems combine the advantages of high biomass concentration, high specific surface area for mass transfer, and low operating cost.

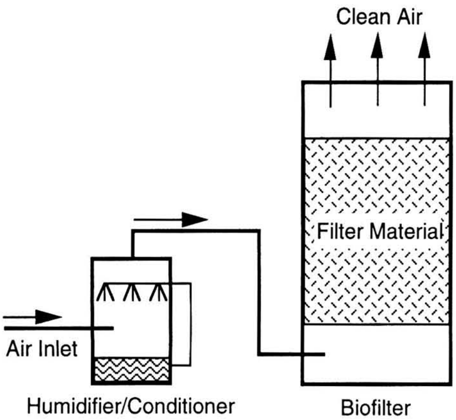

FIGURE 1. Biofilter schematic.

FIXED-FILM BIOTREATMENT SYSTEMS

Figure 1 is a schematic of a biofiltration system. Biofiltration is a process that utilizes microorganisms immobilized in the form of a biofilm layer on an adsorptive filter substrate such as compost, peat, or soil. As a contaminated vapor stream passes through the filter bed, pollutants are transferred from the vapor to the biolayer, and are oxidized.

The simplest form of biofiltration system is the soil bed, where a horizontal network of perforated pipe is placed about two or three feet below the ground [*1*, *2*]. Vapor contaminants are pumped through the piping, flow upward through the soil pores, and are oxidized by microorganisms present within the soil. More sophisticated enclosed units allow for the control of temperature, bed moisture content, and pH to optimize degradation efficiency.

Biofiltration has been used for many years for odor control (H_2S and related sulfur compounds, esters, etc.) at rendering plants and slaughter houses in Germany, the Netherlands, the United Kingdom, Japan, and to a limited extent in the United States. The use of biofilters to degrade more complex volatile emissions from chemical plants has occurred only within the last few years. Biofilters and soil beds have been shown to be effective for treating aromatics such as styrene and toluene [*3*, *4*], aliphatics such as propane and isobutane (5), and more easily degraded compounds such as esters and alcohols [*4*, *6*].

A second type of fixed-film biological system used to treat VOCs is the biotrickling filter (see Figure 2) [*7*]. Biotrickling filters are similar to biofilters, but contain conventional scrubber packing material instead of compost or peat, and operate with a recirculated liquid flowing over the packing. Only the recirculating liquid is initially inoculated with microorganisms, but a biofilm layer establishes itself on the packing shortly after start-up.

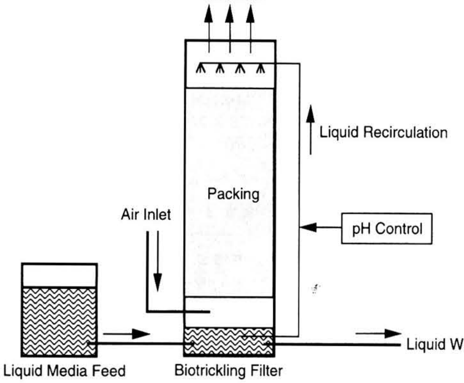

FIGURE 2. Biotrickling filter schematic.

The pH of the recirculating liquid within biotrickling filters is easily monitored and controlled by the automatic addition of acid or base. The pH within biofilters is controlled only by the addition of a solid buffering agent to the packing material at the beginning of operation. Once this buffering capacity is exhausted, the filter bed is removed and replaced with fresh material. For the biodegradation of halogenated contaminants, biofilter bed replacement can be quite frequent. Therefore, biotrickling filters are more effective than biofilters for the treatment of readily biodegradable halogenated contaminants such as methylene chloride.

PERFORMANCE CHARACTERISTICS OF FIXED-FILM SYSTEMS

Operating Regimes

Biofilters

Figure 3 shows bench-scale biofilter performance results for the treatment of air contaiminated with styrene at a nominal bed residence time (bed volume/vapor flow rate) of 1 minute. For the packing used, the maximum volumetric performance (also called elimination capacity) was approximately 70 g/m^3 packing·hr. At styrene loading rates of less than 70 g/m^3 packing·hr, greater than 95% degradation was achieved. Figure 4 shows analogous results for the treatment of air contaminated with ethanol, a contaminant which is degraded three times faster in dilute liquid culture than styrene. The maximum volumetric performance of the biofilter bed for ethanol degradation was approximately 175 g/m^3 packing·hr. At ethanol loading rates of less than 100 g/m^3 packing·hr, greater than 95% degradation was achieved.

A number of simple mathematical models have been developed to help explain and predict biofilter performance as a function of residence time and inlet contaminant concentration. Elimination rates have been approximated by zero-order kinetics [*4*], first-order kinetics [*8*, *9*], and saturation kinetics [*5*]. The data from Figures 3 and 4 were fit to a simple fixed-

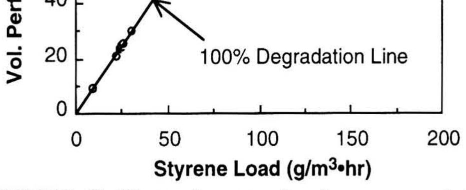

FIGURE 3. Biofilter performance for styrene removal at a vapor residence time of 1.0 min. Volumetric performance (grams styrene degraded per m^3 packing per hr) is plotted as a function of styrene load (grams styrene fed per m^3 packing per hr). Points cannot fall above the 100% degradation line.

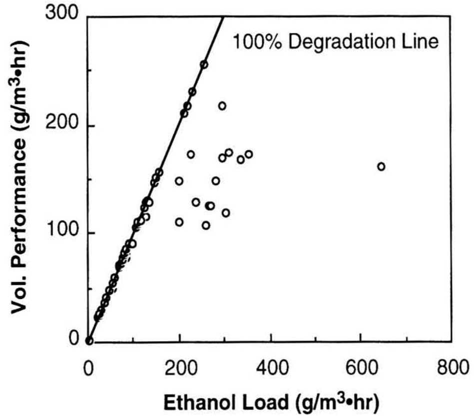

FIGURE 4. Biofilter performance for ethanol removal at a vapor residence time of 1.0 min. Volumetric performance (grams styrene degraded per m^3 packing per hr) is plotted as a function of ethanol load (grams styrene fed per m^3 packing per hr). Points cannot fall above the 100% degradation line.

film, zero-order intrinsic kinetics model for biofilters developed by Van Lith *et al.* [*10*]. This model applies rigorously only in the high contaminant concentration range, but is sufficient for illustrative purposes. The theoretical biofilter performance curves shown in Figure 5 suggest that at economically viable residence times (1 to 1.5 minutes), biofilters can be used for treatment of vapor streams containing up to approximately 1500 μg/L of ethanol or styrene. However, the bench-scale experiments described above were conducted under ideal, steady-state conditions. In real applications, fluctuating contaminant loads and the presence of multiple contaminants can have a dramatic effect on biofilter performance.

Biotricking Filters

Biotricking filters, possibly due to higher internal biomass concentrations, may offer greater performance than biofilters at high contaminant loadings. At a 0.5 minute vapor residence time, the maximum concentration of styrene that can be degraded with 90% efficiency using biotrickling filters is two times higher than can be degraded using biofilters [*11*]. Likewise, the maximum concentration of benzene that can be degraded with 90% efficiency using biotrickling filters is three times higher than can be degraded using biofilters (data not shown).

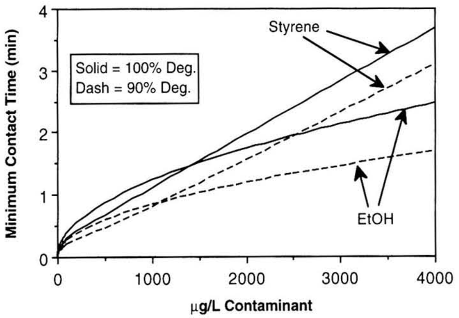

FIGURE 5. Theoretical biofilter performance curves for styrene and ethanol. The data from figures 3 and 4 were fit to a simple fixed-film, zero-order intrinsic kinetics model for biofilters.

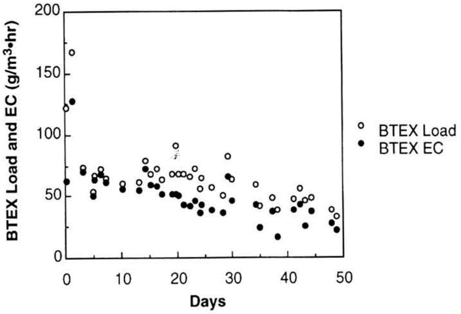

FIGURE 6. Biofilter performance on BTEX/gasoline-contaminated air. BTEX load and elimination capacity (EC) are plotted as a function of time for a vapor residence time of 1.0 min.

Treatment of Mixed Waste Streams

Many industrial discharges are composed of complex mixtures of chemical compounds. The treatment of these waste streams is frequently more difficult than the treatment of waste streams containing a single component. The pollution control industry therefore places a premium on technologies able to handle complex mixtures of compounds as well as fluctuations in concentration.

For example, biofilters have been suggested as a possible alternative to incineration and carbon adsorption for treatment of vapors extracted from soils contaminated with petroleum hydrocarbons. This possibility was tested at the bench scale by passing benzene, toluene, ethylbenzene, xylenes (BTEX), and gasoline vapors through biofilter columns inoculated with BTEX, gasoline, and aliphatics (isopentane, pentane, and octane) degraders. Figures 6 and 7 show that the BTEX compounds were degraded with high efficiency (75%) within these columns while the lighter aliphatic components of gasoline (gas chromatograph peaks before benzene) were not degraded. Comparable results were obtained using biotrickling filters. These results suggest that the simultaneous removal of BTEX and light-end aliphatics from petroleum hydrocarbon vapors using biofilters may require two or more optimized biofilters

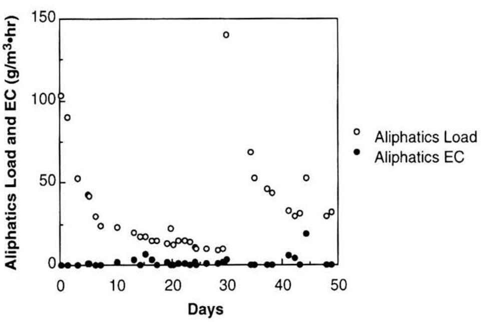

FIGURE 7. Biofilter performance on BTEX/gasoline-contaminated air. Aliphatics load and elimination capacity (EC) are plotted as a function of time for a vapor residence time of 1.0 min.

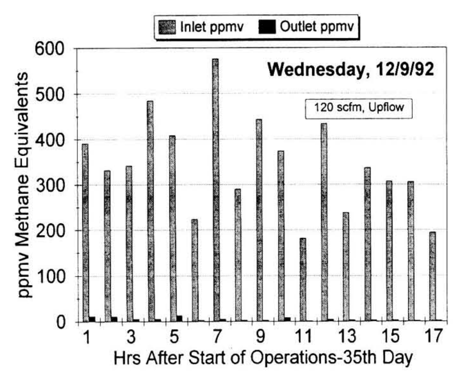

FIGURE 8. Typical average hourly performance of ENVIROGEN's field-pilot biofilter system (30 ft^3 of packing) treating a slip stream of styrene-contaminated air discharged from a spray booth operation. Concentrations are in units of ppmv methane equivalents (μg/L styrene = ppmv methane equivalents X 0.54).

or biotrickling filters in series. Any complex mixture of contaminants with widely different chemical, physical, and biodegradative properties such as petroleum hydrocarbon vapors may require such a sequential and optimized treatment train.

Treatment of Fluctuating Inlet Concentrations

Figure 8 shows the typical average hourly performance of Envirogen's field-pilot biofilter system (30 ft^3 of packing) treatment a slip stream of styrene-contaminated air discharged from a spray booth operation. The concentration of organics in the spray booth effluent stream varied from as high as 1000 ppmv methane equivalents (550 μg/L styrene) to as low as 100 ppmv methane equivalents (55 μg/L styrene) as the spray booth guns were turned on and off repeatedly. These extreme swings in concentration occurred some 20 to 40 times over a typical one hour period. As shown in Figure 8, these minute to minute fluctuations in influent styrene concentration had a negligible effect on system effluent quality. For this application, the biofilter packing was designed to have a high adsorptive capacity for styrene so that movement of styrene through the biofilter bed could be controlled primarily by adsorption onto the packing [*8*]. Movement of high concentrations of styrene through the bed was therefore retarded by the packing, increasing the time available for biodegradation.

CONCLUSIONS

Biofilters and biotrickling filters offer an alternative to conventional air treatment technologies for the treatment of waste streams containing low concentrations of volatile or semi-volatile organics. Biofiltration has been used for many years for odor control (H_2S and related sulfur compounds, esters, etc.) at rendering plants and slaughter houses in Germany, the Netherlands, the United Kingdom, Japan, and to a limited extent in the United States. The use of biofilters to degrade more complex VOC emissions from chemical plants has occurred only within the last few years.

Biotrickling filters have not been used as often as biofilters for the control of VOCs, possibly because they are considered more difficult to operate than biofilters. Biotrickling filters have been considered only for those applications where biofilters would not be appropriate, such as for treatment of halogenated contaminants, where continuous pH monitoring and control are critical.

At economically viable residence times (1 to 1.5 minutes), biofilters can be used for treating vapor streams containing up to approximately 1500 μg/L of readily biodegradable compounds. Biotrickling filters may offer greater performance than biofilters at high contaminant loadings, possibly due to higher internal biomass concentrations. Both systems are best suited for treating vapor streams containing one or two major compounds. If designed properly, biofilters are especially well suited for treating streams that vary in contaminant concentration from minute to minute due to the adsorptive characteristics of the engineered packing.

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Modelling the Fate of Chlorinated Phenols in Wastewater Treatment Plants

W. J. Parker and J. P. Bell
ENVIROMEGA Ltd., 7, Innovation Drive, Hamilton, Ontario L9J 1K3, Canada.
H. Melcer
Wastewater Technology Centre, Burlington, Ontario

The behavior of 2-chlorophenol, 2,4,6-trichlorophenol and pentachlorophenol in activated sludge wastewater treatment plants was investigated at pilot scale. Batch sorption studies along with steady state and dynamic continuous flow experiments were performed to determine partitioning between the liquid and solid phases and biodegradation rate coefficients. A mechanistic mass balance based model was employed as a framework with which sorption and biodegradation coefficients were estimated by model fitting of experimental data for each compound.

Pentachlorophenol was adsorbed to the greatest extent and biodegraded the least with values for the sorption and biodegradation coefficients ranging from 0.6–9.6 L/g and 0.021–0.058 L/g·hr respectively. There was evidence of a dependence of biodegradation rate upon sludge age for pentachlorophenol. The sorption and biodegradation coefficients for 2,4,6-trichlorophenol were estimated in the range 0.11–0.71 L/g and 0.041–0.042 L/g·hr respectively. 2-Chlorophenol was sorbed the least and biodegraded to the greatest extent with sorption and biodegradation coefficients of 0.06 L/g and 0.23 L/g·hr respectively.

INTRODUCTION

Increasing concerns about the emission of contaminants to the environment has led to a demand for knowledge about the behavior of these compounds in wastewater treatment plants. This requires an understanding of degradation rates and as well intermedia transport between the liquid, gas and solids states. More stringent regulations which have evolved as a result of these concerns have led regulators, designers and owners of wastewater treatment plants to require models predicting contaminant behavior, thereby allowing optimization of plant design and control. These models can be used to assess the impact of fluctuations in input concentration on effluent, sludge and offgas streams and can also be employed to establish limits on treatment plant influent loadings based upon allowable effluent loadings.

Models which can perform these functions must contain kinetic expressions which are representative of each removal mechanism. These expressions must be incorporated into hydraulic models which accurately represent the individual processes in the flowsheet. After the overall model has been derived, it is essential that it be calibrated under realistic conditions to obtain accurate estimates of the model coefficients. Over the last 5 years, Enviromega along with Environment Canada's Wastewater Technology Centre has focused on developing a mechanistic model based upon these concepts and the result of this research is the TOXCHEM model (Bell *et al.* [*3*], Bell and Melcer [*2*]).

A portion of the research consisted of performing bench and pilot scale research to estimate the pertinent treatment parameters for the chlorophenol compounds. The chlorophenols are frequently detected and are of concern in both municipal and industrial wastewater treatment plants (Burns and Roe [4], Canviro Consultants [7]). The release of chlorophenols to sewers results from their use in various processes or as process byproducts. Pentachlorophenol and 2,4,6-trichlorophenol are commonly used as pesticides and bactericides, while 2-chlorophenol is an intermediate of dye production and synthesis of higher chlorophenols [9]. All of these compounds are commonly found in the process effluents of bleached kraft pulp mills [13].

Previous treatability studies of chlorophenols have typically studied degradation of these compounds as sole carbon sources and at concentrations in the mg/L concentration range [12]. However, these compounds are generally present in the μg/L range [5] in a complex organic carbon matrix such as municipal sewage. Under such conditions, these compounds will be degraded as secondary substrates with likely substantially different factors influencing biokinetic rates. It is therefore important to perform treatability studies and estimate model parameters under these more realistic conditions. This paper describes research performed to determine the fate of chlorophenols in municipal activated sludge plants.

MODEL DESCRIPTION

The TOXCHEM model is a mass balance based model designed to predict the behavior of contaminants in wastewater treatment plants under either steady state or dynamic conditions. The model incorporates intrinsic reaction rates to predict removal due to surface volatilization, air stripping, biodegradation and biosorption in grit chambers, aeration basins and primary and secondary clarifiers. However, in this research, removal of chlorophenols by biodegradation and sorption in the aeration basin and secondary clarifier, only, were of interest. In the model, biodegradation was represented by mixed second order kinetics in biomass and liquid phase contaminant concentrations, and therefore:

$$r_b = k_b X C \qquad (1)$$

where:

r_b = biodegradation rate, μg/L·h,
k_b = biodegradation rate constant, L/g·h,
X = biomass concentration, g/L,
C = contaminant concentration, μg/L.

This form of removal kinetics has been found to be most accurate for representing trace contaminants present in a complex wastewater matrix [15].

Sorption onto biosolids was represented by a linear isotherm in contaminant concentration.

$$q = K_p C \qquad (2)$$

where:

q = concentration of contaminant in solid phase, μg/g,
K_p = sorption partition coefficient, L/g.

This equation is valid when contaminants are present at low concentrations as would be found in municipal wastewater treatment plants. For the purposes of the model derivation it was assumed that sorption was reversible and that sorption and desorption are instantaneous.

The mass balance on the aeration basin assumed completely mixed conditions to yield the following equation:

$$QC_o + RQ(1 + X_r K_p)C_1 - Q(1 + R)(1 + XK_p)C_1 - Vk_b X C_1 = V(1 + XK_p)\frac{dC_1}{dt} \qquad (3)$$

where:

Q = wastewater flow rate, L/h,

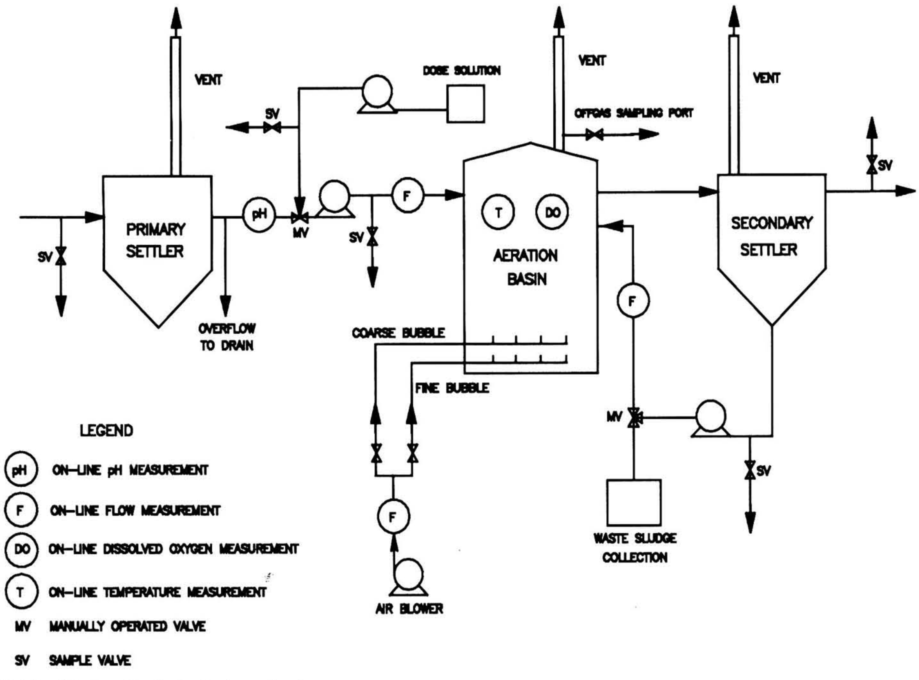

FIGURE 1. Pilot activated sludge plant.

C_o = influent contaminant concentration, μg/L,
C_1 = aeration basin effluent concentration, μg/L,
R = recycle ratio, dimensionless,
X_r = return sludge VSS concentration, g/L,
V = aeration tank volume, m^3,
t = time, h.

The mass balance on the secondary clarifier assumed completely mixed conditions, negligible biodegradation and that the return activated sludge was in equilibrium with the influent contaminant concentration to yield the following equation:

$$Q(1+R)(1+K_pX)C_1 - Q(1+K_pX_e)C_2 - QR(1+K_pX_r)C_1 = V_c(1+K_pX_e)\frac{dC_2}{dt} \quad (4)$$

where:

V_c = secondary clarifier volume, m^3,
X_e = clarifier effluent VSS concentration, g/L,
C_2 = clarifier effluent contaminant concentration, μg/L.

In the experimental research described in this paper, the pilot plant was subjected to a series of three step inputs of contaminants in the 4 day SRT experiments and two step inputs in the 10 day SRT experiment. The differential equations were solved numerically employing a fourth order Runge-Kutta solver with adaptive step size control. The solved equations were coupled to the non-linear regression routine UWHAUS to estimate the sorption and biodegradation coefficients from the experimental data.

MATERIALS AND METHODS

Bench scale batch tests and pilot scale continuous flow experiments under steady state and dynamic conditions were performed to determine sorption partitioning and biodegradation coefficients for selected chlorophenols. The batch tests were performed to independently obtain sorption partitioning coefficients by isotherm analysis. The steady state continuous flow experiments were performed with chlorophenols dosed into tapwater in the pilot plant to evaluate recoveries of the compounds in the absence of biomass and to assess the potential for stripping of the compounds. The dynamic continuous flow experiments were performed with chlorophenols dosed into primary clarifier effluent to determine the sorption partitioning and biodegradation coefficients in the presence of an unacclimated biomass.

Batch Sorption Experiments

In the batch experiments, 750 mL of mixed liquor from the Burlington, Ontario wastewater treatment plant was dosed with various quantities of PCP, TCP, and 2-CP over a range of concentrations from 0.05 to 2.0 mg/L. After a one hour contact time in a glass beaker at a temperature of 20°C, samples of the solutions were collected for analysis. Both filtered and unfiltered samples were analyzed for chlorinated phenols.

Continuous Flow Pilot Plant Experiments

The activated sludge pilot plant consisted of a 5 m^3, 3 m deep aeration basin with primary and secondary settlers each 1.5 m diameter and 2 m deep (Figure 1). Provision was made for the continuous dosing of contaminants into the primary effluent. The aeration basin was equipped with fine pore diffused aerators with the pressure and temperature of the air entering the diffusers and the air leaving the aeration basin continuously monitored with thermocouples and pressure gauges. The air entering the diffusers was generally under moderate pressure (approximately 5 psig). The volumetric air flow rate entering the diffusers was measured using a rotameter: Plant influent and return activated sludge (RAS) flowrates were continuously monitored using magnetic flowmeters. Influent temperature, pH and dissolved oxygen concentration in the aeration basin were also continuously monitored.

In the steady state experiments, a solution of four chlorinated phenols (2-chlorophenol (2-CP), 2,4-dichlorophenol (DCP), 2,4,6-trichlorophenol (TCP), and pentachlorophenol (PCP)) was injected into the influent to the aeration tank which was being fed tap water. The dosing solution consisted of the described chemicals dissolved in distilled water at a concentration of 200 mg/L. The injection was continued at a constant rate for approximately 24 hours to allow attainment of steady state conditions. Influent, effluent, and off-gas samples were then collected and analyzed. Off-gas was analyzed by bubbling a side stream of the off-gas through both acetone and sodium hydroxide solution impingers. The pilot plant was operated with a water flow of 1.11 m^3/hr and an air flow of 17 m^3/hr during these experiments.

During the dynamic experiments, the pilot plant was fed degritted municipal sewage from the Burlington, Ontario wastewater treatment plant which is located adjacent to the Wastewater Technology Centre. The pilot plant operating conditions are presented in Table 1. For the first two experiments, the pilot plant was operated with a solids retention time (SRT) of 4 days while an SRT of 10 days was maintained for the third experiment. In the first dynamic experiment, a dosing solution consisting of pentachlorophenol at a concentration of 200 mg/L in distilled water was injected into the aeration tank influent for 24 hours to provide a target influent concentration of 100 μg/L. The flow rate of the dose injection was increased at 24 hours to approximately double the influent PCP concentration to a target value of 200 μg/L. After another 24 hours, the dose injection was shut off. Final clarifier effluent samples were collected every hour for 72 hours with an automatic sampler starting at the beginning of the first injection. Effluent samples selected at intervals between 2 and 5 hours were analyzed for chlorinated phenols and related compounds. In addition, periodic grab samples of the aeration tank in-

Table 1 Average Pilot Plant Operating Characteristics During Dynamic Experiments

Parameter/Experiment No.	1	2	3
Wastewater Flow Rate, L/h	810	810	810
Return Sludge Flow Rate, L/h	300	300	300
Air Flow Rate, L/h	17000	17000	27000
Sludge Wasting Rate, L/h	17.7	17.7	4.4
Mixed Liquor Suspended Solids, g/L	1.6	1.3	2.1
Mixed Liquor Volatile Suspended Solids, g/L	1.3	1.1	1.7
Effluent Suspended Solids, mg/L	18.7	16.0	12.6
Return Sludge Suspended Solids, g/L	3.7	3.9	8.9
Return Sludge Volatile Suspended Solids, g/L	3.2	3.1	6.9

fluent, mixed liquor, and return sludge were analyzed. Five samples were filtered and compared to non-filtered samples to quantify partitioning between the solid and liquid phases. A second dynamic experiment, using similar procedures, was carried out with TCP in the dosing solution. The pilot plant was operated without dosing for a period of five days between the PCP and TCP experiments.

In the third dynamic experiment, the pilot plant aeration tank was dosed with a solution containing PCP, TCP, and 2-CP, at a concentration of 200 mg/L in distilled water, to obtain a target aeration basin concentration of 100 μg/L of each compound. The dosing was continued at a constant rate for approximately 72 hours after which the dosing was stopped. Samples of secondary clarifier effluent were collected at intervals of 3 to 5 hours over a period of 115 hours from initiation of dosing. Grab samples were taken in a fashion similar to that in the first two dynamic experiments. The pilot plant was operated without dosing for a period of 60 days before the onset of the third dynamic experiment.

In all pilot plant experiments, 30% of the samples were duplicated as field replicates to assess the validity of the sampling techniques employed.

Analytical Techniques

Liquid samples and impinger solutions were analyzed by derivatizing with acetic anhydride, simultaneously extracting with petroleum ether, and identifying and quantitating by GC/ECD or GC/MSD (for monochlorinated compounds) [*11*]. The resulting detection limits were approximately 0.5 μg/L. Filtered samples were vacuum filtered through 1.6 μm Whatman GF/A glass microfibre filters. Volatile suspended solids were analyzed as per Standard Methods [*1*].

RESULTS AND DISCUSSION

Sorption Studies

Sorption of chlorophenols on to biological solids was estimated using data from the dynamic studies by two independent methods and was as well investigated in separate batch tests. During the dynamic experiments filtered and non-filtered samples of mixed liquor and clarified effluent were analyzed for chlorophenols to estimate partitioning between the liquid and solid phases. The concentration of chlorophenols sorbed on to the solids was calculated as:

$$q = (C_{\text{unfil}} - C_{\text{fil}})/\text{VSS}$$

where,

q = solid phase contaminant concentration, μg/g,
C_{unfil} = contaminant concentration in unfiltered solution, μg/L,
C_{fil} = contaminant concentration in filtered solution, μg/L,
VSS = volatile suspended solids concentration, g/L.

Table 2 Sorption Partition Coefficients for Chlorophenolics

	Sorption Partition Coefficients (L/g) ±95% Confidence Limits		
Compound	Dynamic Isotherm Analysis	Dynamic Model Fit	Batch Isotherm Analysis
PCP	9.6±4.8	0.60±0.05 1.54±0.19	1.2±0.2
TCP	0.71±0.68	0.22±0.12 0.37±0.20	0.11±0.03
2-CP	N.A.	N.A.	0.06±0.006

N.A.—Insufficient Data

A linear sorption isotherm equation was fitted to the data by linear regression of equation 2. The estimated sorption partition coefficients along with confidence intervals obtained from this analysis for PCP and TCP are presented in Table 2. Insufficient liquid phase concentration data were available to calculate the partition coefficients for 2-CP.

The partition coefficients were also estimated by fitting the mass balance model (Equations 3 and 4) to the dynamic data using the non-linear regression routine UWHAUS. The estimated values for the partition coefficients along with the confidence intervals obtained by this procedure are presented in Table 2.

Sorption partition coefficients for PCP, TCP and 2-CP were independently estimated with the results from the batch tests. The sorbed concentrations and linear isotherms resulting from the batch tests were determined in a fashion identical to that described for the dynamic experiments. Figure 2 presents a sorption isotherm for PCP in mixed liquor resulting from the batch tests. The partition coefficients estimated by this technique for PCP, TCP and 2-CP along with confidence intervals are presented with the results from the dynamic experiments in Table 2.

In comparing the sorption partitioning coefficients which were obtained by the 3 independent methods, it is apparent that the values obtained by isotherm analysis with samples taken during the dynamic experiment demonstrated the greatest degree of variability. The relatively large confidence intervals obtained by this method are a product of the variability in the data and the relatively small number of samples ($n = 5$). The coefficients obtained by fitting of the dynamic model and from the batch adsorption experiments demonstrated less variability about the estimated values for all 3 compounds studied. The consistency of the values obtained for PCP and TCP by the two independent estimation techniques confirms that the partitioning coefficients have been calculated correctly. Dobbs *et al.* [*8*] observed an increase in partitioning to biosolids with an increase in a compound's octanol-water partitioning coefficient (K_{ow}). K_{ow} values of 5.12, 3.69 and 2.15 have been reported for PCP, TCP and 2-CP respectively [*9*]. This trend is also observed in the partitioning coefficients estimated in this study. For example, the batch isotherm analysis yielded K_p values of 1.2, 0.11 and 0.06 L/g for PCP, TCP and 2-CP respectively. Therefore, the results of this study confirm those of Dobbs [*8*].

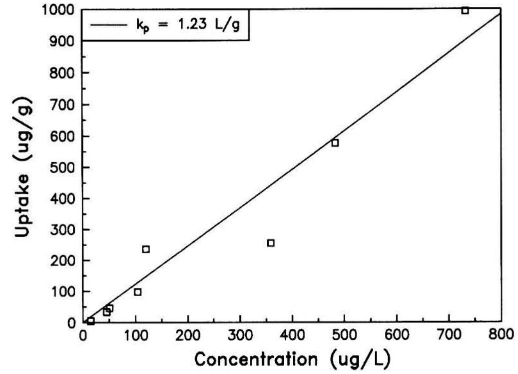

FIGURE 2. Adsorption isotherm for pentachlorphenol in mixed liquor

Table 3 Tap Water Experiments

Compound/Experiment No.	Mass Balance Closure (%) 1	2	3	Average
2-CP	102	—	154	128
DCP	112	—	124	118
TCP	97	—	100	98
PCP	97	100	127	108

Mass Balance and Stripping Studies

Mass balances were performed for the pilot plant operating with dosed tapwater by comparing compound mass fluxes in the aeration basin influent to those in the aeration basin effluent and the offgas stream and are presented in Table 3. The mass balance closures for the four compounds studied ranged from 97 to 154% with an overall average recovery of 112.6%. This degree of recovery was regarded as indicative of satisfactory sampling and analytical techniques. The 4 compounds were not detected in the offgas stream indicating that stripping and volatilization were not significant removal mechanisms.

Biodegradation Studies

Influent and effluent chlorophenol concentrations resulting from the three dynamic experiments were employed in the mass balance models along with UWHAUS to estimate the biodegradation coefficient (k_b) and the sorption partitioning coefficient (K_p). The estimated sorption partition coefficients were presented in the previous section. The measured influent and effluent concentrations and the concentrations predicted by the calibrated model are presented for PCP and TCP for the 4 and 10 day SRTs in Figures 3–4 and 5–6 respectively. All of the effluent concentrations of 2-CP were below the analytical detection limits (0.5 μg/L), and therefore, are not presented graphically. The estimated biodegradation parameters along with 95% confidence intervals which were obtained from the calibration procedure are presented in Table 4.

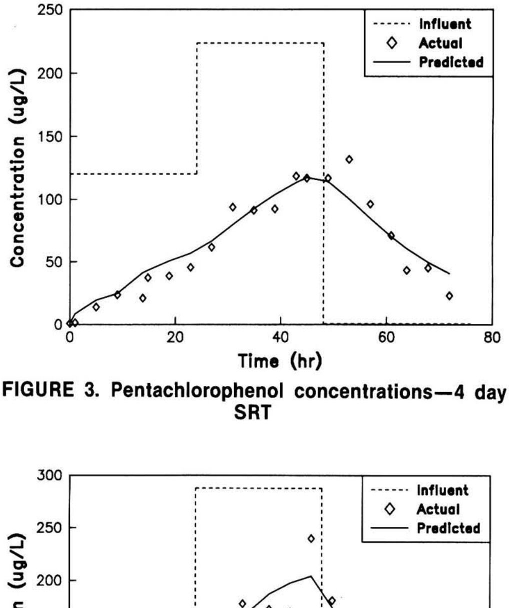

FIGURE 3. Pentachlorophenol concentrations—4 day SRT

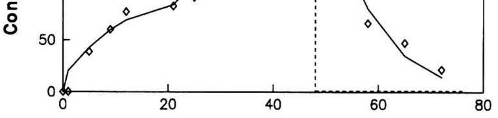

FIGURE 4. 2,4,6-Trichlorophenol concentrations—4 day SRT

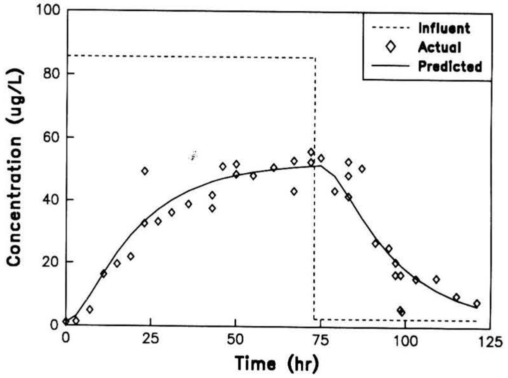

FIGURE 5. Pentachlorophenol concentrations—10 day SRT

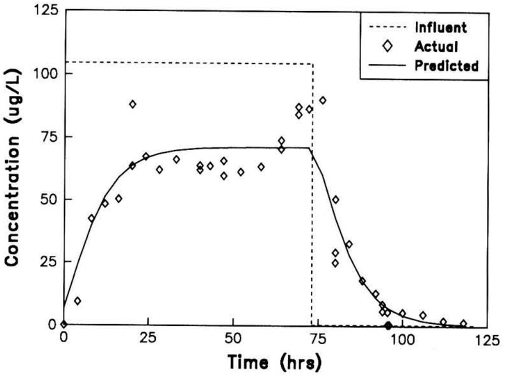

FIGURE 6. 2,4,6-Trichlorophenol concentrations—10 day SRT

A concern when dosing a mixture of phenols with various levels of chlorine substitution in biological systems, as performed in the third dynamic experiment, is the formation of the less substituted compounds, as metabolic breakdown products, from more highly substituted compounds. For example,

Table 4 Biokinetic Rates of Chlorophenol

Compound	Biodegradation Rate (L/g·hr) 4 d SRT	10 d SRT
PCP	0.021 ± 0.008	0.058 ± 0.007
TCP	0.042 ± 0.012	0.041 ± 0.008
2-CP	N.A.	0.23 ± 0.14

N.A.—Not Available.

2-CP and TCP could potentially be formed from degradation of PCP, thereby invalidating the mass balance calculations. Therefore, in the first dynamic experiment, with PCP fed alone, TCP and 2-CP were monitored as potential breakdown products while in the second experiment with TCP fed alone, 2-CP was monitored as a potential breakdown product. The concentrations of these compounds were found to be negligible at all times, and therefore, the mass balances performed in the third dynamic experiment were assumed to be valid since there was no formation of the target compounds in the single compound studies.

It is apparent that the model, when calibrated, is capable of emulating the behavior of chlorinated phenols in municipal wastewater treatment plants. This is reflected in the excellent fit between predicted and observed effluent concentrations in all cases. The high accuracy of the estimated parameters is reflected in the narrow confidence limits which are, in most cases, an order of magnitude lower than the estimated parameters.

For PCP, the estimated biodegradation rate constants of 0.021 ± 0.008 L/g·h and 0.058 ± 0.007 L/g·h for the 4 day SRT and 10 day SRT experiments, respectively, generally agree with that of Coburn *et al.* [7] who reported a range of biodegradation rate constants of 0.063 – 5.38 L/g·h. It should be noted that some of the investigations which were referenced by Coburn [7] were not conducted under conditions typical of operating activated sludge plants (i.e. unacclimated biomass, low influent concentrations). As expected with an unacclimated system, the biodegradation rates estimated in this study are at the low end of the reported range. The biodegradation rates observed at the 4 day SRT are significantly lower than those at the 10 day SRT.

For TCP, the estimated biodegradation rate constants of 0.042 ± 0.012 L/g·h and 0.041 ± 0.008 L/g·h for the 4 day SRT and 10 day SRT experiments respectively, generally agree with those of Coburn *et al.* [7] whom reported a range of biodegradation rate constants of 0.007 – 0.256 L/g·h. Again, as expected in an unacclimated system, the biodegradation rate for TCP is at the lower end of the range. The treatability parameters estimated at a 4 day SRT and a 10 day SRT appear to be reasonably consistent, suggesting that the parameters were essentially independent of SRT.

The lack of response in biodegradation rate to SRT for TCP differs from that of PCP where a higher SRT resulted in a higher biodegradation rate. This behavior indicates that, any changes in the microbial population which resulted from a longer SRT, did not produce a consortium with a greater ability to biodegrade TCP. However, these changes in biomass composition did enhance the ability to biodegrade PCP. This has significant engineering implications for the operation of wastewater treatment plants to enhance the removal of pentachlorophenol.

The effluent concentration values for 2-CP were near or below the analytical detection limit. The data suggest that 2-chlorophenol was almost completely biodegraded in the pilot plant system. The biodegradation rate constant estimated from the dynamic experiment was 0.23 L/g·h±0.14. First order biodegradation rate constants for 2-CP were not available in the literature. Pitter [*14*] reported a zero order concentration, first order biomass, biodegradation rate constant for 2-CP of 14.85 mg/g·h. If the biomass concentration observed in this study is employed with the Pitter [*14*] rate constant, the predicted rate of biodegradation is substantially higher than the observed rate. Since most effluent values were near the detection limit, it is likely that there is excess capacity for biodegradation of 2-CP and that the rate constant determined in this study is a minimum value.

It is apparent that the order of biodegradation rates for the chlorophenols studied is 2-CP > TCP > PCP. This order is consistent with previous aerobic biodegradation studies in that increased chlorine substitution resulted in decreased biodegradation rates (Kobayashi and Rittmann [*10*], Sahm *et al.* [*16*]).

CONCLUSIONS

The behavior of chlorophenols in activated sludge plants was examined at pilot scale and the resulting data were employed to determine the pertinent model parameters in the TOXCHEM model. After calibration, a mass balance based model with intrinsic mixed first order biodegradation rates and linear sorption partitioning was found to emulate the behavior of chlorophenols well.

The sorption of chlorophenols on to biosolids was estimated from both the dynamic pilot plant experiments and also in separate batch tests with substantial differences between the results of experimental techniques in some cases. Pentachlorophenol was sorbed to the greatest extent with the estimated partition coefficients ranging from 0.60 to 9.6 L/g for volatile suspended solids. 2,4,6-Trichlorophenol was sorbed to a lesser estent with estimated partition coefficients of 0.11–1.11 L/g for similar solids. 2-Chlorophenol was the least sorbed of the compounds studied with an estimated partitioning coefficient of 0.06 L/g.

The removal of chlorophenols by volatilization and air stripping was found to be negligible and therefore rate coefficients were not determined.

Pentachlorophenol was the least biodegraded with mixed first order rate coefficients of 0.021 and 0.058 L/g·hr for the 4 and 10 day SRTs respectively; suggesting that the removal is dependent upon sludge age. 2,4,6-Trichlorophenol was degraded at a higher rate with rate coefficients of 0.042 and 0.041 L/g·hr for the 4 and 10 day SRTs respectively; suggesting that the biodegradation is independent of sludge age over the range studied. 2-Chlorophenol was degraded at the highest rate with most effluent concentrations below the detection limits. A rate coefficient of 0.23 L/g·hr was estimated for the 10 day SRT.

ACKNOWLEDGEMENTS

The research described in this paper was funded by Environment Canada.

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Update on VOC MACT Standards

Paul C. Siebert
Roy F. Weston, Inc., 1 Weston Way, West Chester, Pennsylvania

INTRODUCTION

Title III of the Clean Air Act Amendments of 1990 (CAAA) [*3*] changed the method of operation and drastically increased the scope of federal air toxic provisions. The major thrust of this Congressional restructing of the air toxic or hazardous air pollutant (HAP) provisions of the Clean Air Act was the speedier implementation of regulations limiting emissions of air toxics. The major focus is now maximum available control technology (MACT). The method and means of determining MACT differs significantly from the regulatory development of previous national emission standards for hazardous air pollutants (NESHAPs). In particular, the consideration of control technology and cost has changed. This paper attempts to outline the basic structure of CAAA HAP programs and to provide an update of the status of the development of the implementing regulations, particularly those regarding VOC emissions. The major areas of the HAP programs are as follows:

- Determination of MACT;
- Demonstration of early reductions;
- Preparation of permit applications;
- Determination of best technology and practice by state agencies if MACT is not defined federally;
- Assessment of residual risk;
- Production and mitigation of accidental releases.

These areas will be discussed in the corresponding sections of this paper.

DETERMINATION OF MACT

As mentioned previously, the major thrust of the air toxics provisions of the CAAA was to enable and mandate the promulgation of regulations for a large number of air toxics in a much shorter time frame than the development of previous NESHAPs. Under the Clean Air Act of 1970 [*1*], as amended in 1977 [*2*] (the Act), the development and promulgation of NESHAPs was required to follow a rather lengthy and arduous path that was subject to several general criteria that became the focus of regulatory and judicial interpretations and subsequent delays. Therefore, during the years until 1990 only a small number of NESHAPs were promulgated for a handful of hazardous air pollutants. The main provisions of the Act (in Section 112) that brought about this rather ponderous process were the following:

- The requirement that a pollutant had to go through a rather lengthy, and often contested, process of being listed as a hazardous air pollutant, "which causes, or contributes to, air pollution which may reasonably be anticipated to result in an increase in mortality or an increase in serious, irreversible, or incapacitating reversible, illness". This listing process had to be completed before standards could be developed (which process in itself required numerous internal EPA, interagency, and public review steps).
- The requirement that NESHAPs "provide an ample margin of safety to protect the public health" without any other guidance so that the regulatory development process could not consider cost (as was permitted and required for the technology-based new source performance standards [NSPS]).

The first difficulty was removed by Congress specifying both an initial 189 (actually 190 due to a clerical error) substances as air toxics and a detailed regulatory agenda. The removal of the second difficulty is the purpose of the MACT determination process outlined in the CAAA. MACT is defined as the "maximum degree of reduction in emissions ... taking into consideration the cost of achieving such emission reductions and any non-air quality, health and environmental impact and energy requirements ... achievable for new and existing sources." The procedure for determining MACT was also established by Congress. For new sources, MACT for a source category is to be the control achieved in practice by the best controlled similar source. For existing sources, MACT is required to be the average of the top 12% best controlled sources in the source category, excluding those sources utilizing technology considered the lowest achievable emission rate (LAER) within 18 months of proposal or 30 months of promulgation. If there are fewer than 30 sources in the source category, MACT for existing sources is to be the average emission level of the five best performing sources. MACT can also be achieved by process and material modifications in addition to the emission, design, equipment, work practice, or operational standards permissible for NESHAPs. The key points of the old and new methods of developing standards for hazardous air pollutants are compared in Table 1.

The end result of these legislative mandates is that the development of MACT standards is more similar to the development of a NSPS than to previous NESHAPs. Although NESHAPs before the CAAA were not to consider cost, the analysis and decision had to consider cost in some fashion in order to ascertain what level of control and regulatory applicability was warranted for the expected level of emission re-

Table 1 Comparison of NESHAP Development Under the Clean Air Acts of 1977 and 1990

Clean Air Act as Amended in 1977	Clean Air Act as Amended in 1990
• Individual listing of air pollutants as hazardous. —based on expectation of increase in mortality or serious illness —lengthy process —often contested	• 190 compounds listed as hazardous in the act. —provisions to add or delete compounds.
• NESHAPs to "provide an ample margin of safety to protect public health" —risk-based —no consideration of cost —gradually adopted risk management approach —standards contested technically & judicially	• MACT standards based on "maximum degree of achievable reduction" —technology-based —development procedure/criteria defined —schedule for promulgation —considers cost of control
	• Residual risk standards —if MACT not provide an "ample margin of safety" —risk-based —time schedule —no consideration of cost

ductions and corresponding health benefits. Over time the EPA developed a risk management approach that considered cost effectiveness of regulatory strategies in reducing health impacts of a pollutant while giving credit for reductions in criteria (nontoxic) pollutants (e.g., dollars per cancer incidence resulting from benzene emission reductions while giving credit at a specified value(s) in dollars per ton of VOC reduction). In the CAAA Congress recognized the appropriateness of considering cost as well as the difficulties and delays of having to base standards on a risk management approach often based upon contended risk estimates. Therefore, a more streamlined approach was designed consisting of the more swiftly implemented technology-based MACT standards followed within eight years by residual risk standards, if deemed necessary to provide an ample margin of safety.

The development of MACT standards to date appears to be taking the direction of establishing the available technology according to the legislative guidelines and then determining applicability criteria for the sources that must apply the technology based on cost and other considerations. Thus, the control technology analysis is focused on surveying the industry, equipment vendors, and state and local agencies to gather information on the technology in use and its effectiveness. The results of the survey are then assessed to determine the maximum available technology based on the appropriate definition in the CAAA. After the MACT control level is determined, an analysis of cost and other impacts is conducted to evaluate and develop applicability criteria for the MACT standard. The determination of applicability criteria is based on a case-by-case assessment of reasonableness with regard to cost effectiveness of emission reduction, cost benefit of environmental/health effects, and economic impacts on product pricing and individual facilities. Regulatory decisions are generally based on the points in the case-by-case analysis where there is distinct break or change in the relative costs and benefits of applying the standard, rather than on any predetermined cost effectiveness or other criteria that is used for all source types and pollutants. Therefore, the technology and cost analyses are much more similar to that of an NSPS than a NESHAP based on a risk management analysis.

EPA received the first petition to delete compounds from the list of HAPs from the Chemical Manufacturers Association (CMA) on October 16, 1991. The petition requested that five specific glycol ethers be deleted. Based on its initial review, EPA determined that the petition did not contain enough data on exposure to emissions of these glycol ethers to determine risks to the public health and the environment. CMA and EPA have had subsequent meetings to discuss further actions. Because the direction of MACT standards development is toward source category standards rather than pollutant standards, EPA does not expect to make many modifications to the list of HAPs.

Several milestones toward the general development of MACT standards have been reached. A preliminary draft list of source categories and subcategories for MACT development was published on June 21, 1991 (56 FR 28548) [16], followed by the final list on July 21, 1992 (57 FR 31576) [5]. Based on commends received regarding the draft list and further Agency review, EPA substantially reduced the number of source categories in the final list. For example, the synthetic organic chemical manufacturing industry (SOCMI) category was consolidated from about 400 categories into a single category in order to clarify the category definition and to expand the opportunity to consider emissions averaging. In addition, EPA removed some categories where evidence was inadequate to show that at least one source in the category is a major source (e.g., emits at least 10 tpy of one HAP or 25 tpy of any combination of HAPs) and deferred some area source categories (such as small combustion devices) because a finding of a threat to human health or the environment has not made. EPA then published a draft timetable for regulating these "initial" source categories on September 24, 1992 (57 FR 44147) [7]. This timetable is included as Table 2.

A number of NESHAPs have been recently promulgated or proposed. The NESHAP for perchloroethylene dry cleaning facilities was proposed on December 9, 1991 (56 FR 64382) [10]. The availability of additional information regarding possible new equipment was announced on October 1, 1992 (57 FR 45363) [11]. The coke oven MACT standard was proposed on December 4, 1992 (57 FR 57534) after development through regulatory negotiation with participants from state and local agencies, industry, and environmental groups. The final amendments to the NESHAP for benzene emissions from benzene waste operations (Subpart FF of 40 CFR 61) were promulgated on January 7, 1993 (58 FR 3072) [13]. Although this standard regulates hazardous VOC emissions it will not be discussed in this paper. Finally, the hazardous organic NESHAP or HON was proposed on December 31, 1992 (57 FR 62608) [8]. This standard will be outlined as it is likely to set a number of precedents for MACT standards development and for VOC MACT standards in particular.

The HON establishes standards for the synthetic organic chemical manufacturing industry (SOCMI) that are estimated to reduce emissions of 149 of the 190 listed air toxics by an estimated 500,000 tons per year. The source types affected by the HON are storage vessels, process vents, equipment leaks, transfer operations, and wastewater operations. The HON also

Table 2 EPA Draft Timetable for Regulating Categories of Sources of Hazardous Air Pollutants (57 FR 44147; Sept. 24, 1992 [7])

Source Categories with Emission Standards Due by Nov. 15, 1992

Synthetic Organic Chemical Manufacturing Commercial Drycleaning (Perchloroethylene)—Transfer Machines*
Commercial Drycleaning (Perchloroethylene)—Dry-To-Dry Machines*
Commercial Drycleaning (Perchloroethylene)—Transfer Machines
Industrial Drycleaning (Perchloroethylene)—Transfer Machines
Industrial Drycleaning (Perchloroethylene)—Dry-To-Dry Machines

Source Categories with Emission Standards Due by Nov. 15, 1994

Acrylonitrile-Butadiene-Styrene Production
Aerospace Industries
Asbestos Processing*
Butyl Rubber Production
Chromic Acid Anodizing
Chromic Acid Anodizing
Coke Ovens: Charging, Topside and Door Leaks (CAA Mandated Promulgation by December 31, 1992)
Commercial Sterilization Facilities
Commercial Sterilization Facilities*
Decorative Chromium Electroplating
Decorative Chromium Electroplating*
Epichlorohydrin Elastomers Production
Epoxy Resins Production
Ethylene-Propylene Rubber Production
Gasoline Distribution—Stage 1
Halogenated Solvent Cleaners
Halogenated Solvent Cleaners*
Hard Chromium Electroplating
Hard Chromium Electroplating*
Hypalon (TM) Production
Industrial Process Cooling Towers
Magnetic Tapes (Surface Coating)
Methyl Methacrylate-Acrylonitrile-butadiene-Styrene Production
Methyl Methacrylate-Butadiene-Styrene Terpolymers Production
Neoprene Production
Nitrile Butadiene Rubber Production
Non-Nylon Polyamides Production
Petroleum Refineries—Other Sources Not Distinctly Listed
Polyethylene Terephthalate Production
Polybutadiene Rubber Production
Polysulfide Rubber Production
Polystyrene Production
Printing/Publishing (Surface Coating)
Secondary Lead Smelting
Shipbuilding and Ship Repair (Surface Coatings)
Solid Waste Treatment, Storage, & Disposal Facilities (TSDF)
Styrene-Acrylonitrile Production
Styrene-Butadiene Rubber and Latex Production
Wood Furniture (Surface Coating)

Source Categories With Emission Standards Due by Nov. 15, 1997

Acetal Resins Production
Acrylic Fibers/Modacrylic Fibers Production
Aerosol Can-Filling Facilities
Amino Resins Production
Auto and Light Duty Truck (Surface Coating)
Benzyltrimethylammonium Chloride Production
Butadiene Dimers Production
Carboxymethylcellulose Production
Cellophane Production
Chelating Agents Production
Chloroneb Production
Chlorine Production
Chromium Chemicals Manufacturing
Chromium Refractories Production
Cyanuric Chloride Production
Ferroalloys Production
Flexible Polyurethane Foam Production
Hydrazine Production
Hydrochloric Acid Production
Hydrogen Cyanide Production

(continued on following page)

Table 2 (continued) EPA Draft Timetable for Regulating Categories of Sources of Hazardous Air Pollutants (57 FR 44147; Sept. 24, 1992 [7])

Hydrogen Fluoride Production
Integrated Iron & Steel Manufacturing
Iron Foundries
Mineral Wool Production
Municipal Landfills
Non-Stainless Steel Manufacturing—Electric ARC Furnace (EAF) Operation
Nylon 6 Production
Oil and Natural Gas Production
Paper and Other Webs (Surface Coating)
Petroleum Refineries—Catalytic Cracking (Fluid and Other) Units, Catalytic Reforming Units, and Sulfur Plant Units
Pharmaceuticals Production
Phenolic Resins Production
Phosphate Fertilizers Production
Phosphoric Acid Manufacturing
Photographic Chemicals Production
Polycarbonates Production
Polyester Resins Production
Polyether Polyols Production
Polymethyl Methacrylate Resins Production
Polyvinyl Acetate Emulsions Production
Polyvinyl Alcohol Production
Polyvinyl Butyral Production
Portland Cement Manufacturing
Primary Aluminum Production
Primary Copper Smelting
Primary Lead Smelting
Publicly Owned Treatment Works (POTW) Emissions (CAA Mandated Promulgation by November 15, 1995)
Pulp & Paper Production
Rayon Production
Reinforced Plastic Composites Production
Rubber Chemicals Manufacturing
Secondary Aluminum Production
Semiconductor Manufacturing
Sewage Sludge Incineration
Sodium Cyanide Production
Stainless Steel Manufacturing—Electric ARC Furnace (EAF) Operation
Stationary Internal Combustion Engines
Stationary Turbines
Steel Foundries
Steel Pickling—HCI Process
Wood Treatment
Wool Fiberglass Manufacturing

Source Categories with Emission Standards Due by Nov. 15, 2000

2,4-D Salts and Esters Production
4,6-Dinitro-o-Cresol Production
4-Chloro-2-Methylphenoxyacetic Acid Production
Alkyd Resins Production
Alumina Processing
Ammonium Sulfate Production—Caprolac-tam by-Product Plants
Antimony Oxides Manufacturing
Asphalt Concrete Manufacturing
Asphalt Processing
Asphalt Roofing Manufacturing
Asphalt/Coal Tar Application—Metal Pipes
Bakers Yeast Manufacturing
Boat Manufacturing
Butadiene-Furfural Cotrimer (R-11)
Captafol Production
Captan Production
Carbonyl Sulfide Production
Cellulose Ethers Production
Cellulose Food Casing Manufacturing
Chlorinated Paraffins Production
Chlorothalonil Production
Clay Products Manufacturing
Coke By-Product Plants
Coke Ovens: Pushing, Quenching and Battery Stacks

(continued on following page)

Table 2 (continued) EPA Draft Timetable for Regulating Categories of Sources of Hazardous Air Pollutants (57 FR 44147; Sept. 24, 1992 [7])

Daethal (TM) Production
Dodecanedioic Acid Production
Dry Cleaning (Petroleum Solvent)
Engine Test Facilities
Ethylidene Norbornene Production
Explosives Production
Flat Wood Paneling (Surface Coating)
Fume Silica Production
Hazardous Waste Incineration
Industrial Boilers
Institutional/Commercial Boilers
Large Appliance (Surface Coating)
Lead Acid Battery Manufacturing
Lime Manufacturing
Maleic Anhydride Copolymers Production
Manufacturing of Paints, Coatings & Adhesives
Metal Can (Surface Coating)
Metal Coil (Surface Coating)
Metal Furniture (Surface Coating)
Methylcellulose Production
Miscellaneous Metal Parts & Products (Surface Coating)
OBPA/1,3-Diisocyanate Production
Organic-Liquids Distribution (Non-Gasoline)
Paint Stripper Users
Phthalate Plasticizers Production
Plastic Parts and Products (Surface Coating)
Plywood/Particle Board Manufacturing
Polymerized Vinylidene Chloride Production
Polyvinyl Chloride & Copolymers Production
Primary Magnesium Refining
Printing, Coating & Dyeing of Process Heaters
Quaternary Ammonium Compounds Production
Rocket Engine Test Firing
Site Remediation
Sodium Pentachlorophenate Production
Spandex Production
Symmetrical Tetrachloropyridine Production
Taconite Iron Ore Processing
Tire Production
Tordon (TM) Acid Production
Uranium Hexafluoride Production
Vegetable Oil Production

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*Denotes area source Category

regulates equipment leaks from seven non-SOCMI processes: styrene/butadiene rubber production, polybutadiene production, chlorine production, pesticide production, chlorinated hydrocarbon use, pharmaceutical production, and miscellaneous butadiene use. Based on regulatory negotiation, MACT has been defined for each source type based on a control efficiency that can be achieved by one or more control or pollution prevention techniques. These reference control technologies, which were selected for each source type based on past and ongoing standards development, are summarized in Table 3, along with the selected reference control technology. Economic and environmental impacts were assessed for model emission sources developed for each source type and assigned to each production process. Regulatory options were developed from combinations of control levels at least as stringent as the Congressionally mandated MACT floor level with various source and chemical applicability criteria. In addition to the goal of maximum achievable emissions reduction, EPA also attempted to achieve the following secondary goals in the HON: overall administrative simplicity, allowing flexibility in implementation in order to reduce costs, encouraging pollution prevention, and ensuring enforceability.

The reference control technology standards apply to all emission sources of a source type having a specified value of a total resource effectiveness (TRE) equation or meeting certain specific criteria regarding the emission source and chemical. The TRE equation approach, which is similar to that used for the SOCMI air oxidation, distillation, and reactor NSPSs, was used for process vents in the proposed HON. For each control device type, a linear equation was developed that considers relevant emission source and chemical characteristics, such as HAP emission rate, and gas stream flowrate, heat content, and total organic compounds (TOC) emission rate. The emission points meeting the specified applicability criteria for the source type are classified as Group 1 emission points; all other emission points are classified as Group 2 emission points.

A novel feature of the proposed HON is the emissions averaging provision, which essentially allows emissions trading between the different emission points at the same facility that are subject to the HON. A facility may choose to control all Group 1 emission points with the reference control technology. Alternatively, a facility-wide equivalent level of emissions reduction may be achieved through a combination of less effective controls on some Group 1 emission points (accumulating

Table 3 Summary of HON Controls

Emission Point	Reference Control Technology	Reference Control Efficiency (%)
Process Vents	• Combustion —Flare —Incinerator —Boiler/Process Heater	98
Storage Vessels	• Internal floating roof • External floating roof • Closed vent system with controls	95
Wastewater	• Controlled transport and storage and steam stripper with controls for stripper vents.	95–98[a]
Transfer Operations	• Combustion —Flare —Incinerator —Boiler • Recovery	98
Equipment Leaks	• Enhanced leak detection and repair • Equipment specifications	80–88[b]

[a] The efficiency for the wastewater stripper is 95–98 percent. The percent HAP reduction from wastewater varies with the compounds and concentrations in the individual streams.

[b] Efficiency varies depending on the equipment in the process unit and other factors.

"debits") and control of Group 1 emission points with technologies rated by EPA as more effective than the reference level, control of Group 2 emission points, and more stringent pollution prevention measures (accumulating "credits"). Emissions averaging does not include equipment leaks and credit generally can not be taken for a reference technology operated at greater than the reference efficiency. EPA is requesting comments on whether emission credits should be discounted by as much as 20%.

The HON also includes detailed specifications of monitoring, recordkeeping, and reporting requirements for operating parameters of each control device. EPA is proposing to allow sources to set site-specific ranges for each device. The parameter monitoring provision was included in response to a requirement in the final operating permits program rule. The proposed type of monitoring is considered "enhanced monitoring" because the data generated can be used to determine compliance.

The affected industry as well as other interested parties have the opportunity to comment on EPA's collected data, analyses, and proposed standards. It is to the industry's advantage to submit data on emissions, and the feasibility, performance, and cost of various control techniques and pollution prevention measures as early as possible so that they are considered in EPA's initial standards development. Therefore, the primary focus of the comments would be expected to be the appropriateness of the assumptions used in developing the model emission sources and in the economic and impact analyses and whether the emission reductions have been achieved in practice, especially with the design and cost assumed. One of the most effective ways of presenting such comments is to present an alternative control technology and cost analysis based on what are considered more appropriate assumptions and bases, but using the same standard guidelines and presentation. Industry comments on the practicality and cost of enforcement, monitoring, recordkeeping, and reporting should also provide concrete examples and alternatives rather than general statements.

DEMONSTRATION OF EARLY REDUCTIONS

Title III of the CAAA provides that an emission source of air toxics can obtain a 6-year extension on complying with MACT standards if the source significantly reduces emissions prior to proposal of MACT standards for the source category. Early reductions of 90% of gaseous HAPs or 95% of particulate HAPs are required for the compliance extension. The reductions must be achieved or an enforceable commitment made before the standard is proposed. According to the proposed implementing regulations, the required reduction must be achieved for the most toxic (Category I) high risk pollutants, all high risk pollutants (Categories I & II), and all HAPs. Procedures have been published by EPA for establishing emissions for early reduction programs, including specific guidance for SOCMI (Procedures for Establishing Emissions for Early Reduction Compliance Extensions, Volume 1—Synthetic Organic Chemical Manufacturing, Ethylene Oxide Sterilization, and Chromium Electroplating; EPA-450/3-91-012a; July 1991 [*17*]). As specified in the proposed regulations governing compliance extensions for early reductions, the preferred technique of demonstrating the post-control emission rate is actual measured emissions data. Engineering estimates of emissions (based on engineering principles, emission factors or mass balances) can be used only if they can be demonstrated to be as accurate as emissions testing; no test method is available; testing is technically or economically infeasible; or emissions from that source point are small compared to the total and would have little impact. Thus, for most source categories engineering assessment of control technology and cost will not enter into the permitting process. However, such analyses should be the basis of the facilitiy's decision to pursue early reductions as well as the most cost effective means to achieve the required reductions for the particular emission source.

There is a special provision of the early reduction sections of the amended Act (Section 112(i)(5)(B)) that makes allowance for the short legislative timetable for MACT standards. If a source will be subject to standards proposed before 1994 yet can not achieve the reduction before proposal it can qualify for a compliance extension by making an enforceable commitment to achieve the required reduction. Such an enforceable commitment must include the general plan for reducing emissions. The preamble states, "The description of the planned emission reduction measures does not bind the source to carrying out the plan exactly but should be in sufficient detail to demonstrate that the source owner or operator has given serious consideration to real emission reduction measures that can be implemented to qualify the source for the early reduction

Table 4 List of High-Risk Pollutants[a]

CAS No.	Chemical	Weighting Factor
53963	**2-Acetylaminofluorene**	**100**
107028	Acrotein	100[b]
79061	Acrylamide	10
79107	Acrylic acid	10
107131	Acrylonitrile	10
	Arsenic compounds	100
1332214	Asbestos	100
71432	Benzene	10
92875	Benzidine	1,000
	Beryllium compounds	10
542881	Bis(chloromethyl)ether	1,000
106990	1,3-Butadiene	10
	Cadmium compounds	10
57749	Chlordane	100[b]
532274	**2-Chloroacetophenone**	**100**
	Chromium compounds	100
107302	Chloromethyl methyl ether	10
	Coke oven emissions	10[b]
334883	**Diazomethane**	**10**
132649	Dibenzofurans	10
96128	**1,2-Dibromo-3-chloropropane**	**10**
111444	Dichloroethyl ether	10
79447	**Dimethyl carbamoyl chloride**	**100**
122667	**1,2-Diphenylhydrazine**	**10**
106934	Ethylene dibromide (Dibromoethane)	10
151564	**Ethylenimine (Aziridine)**	**100**
75128	Ethylene oxide	10
76448	Heptachlor	100[b]
118741	Hexachlorobenzene	100[b]
77474	**Hexachlorocyclopentadiene**	**10**
302012	Hydrazine	100
	Manganese compounds	**10**
	Mercury compounds	100[b]
101688	Methylene diphenyl diisocyanate (MDI)	10
60344	**Methyle hydrazine**	**10**
624839	Methyl isocyanate	10
	Nickel compounds	**10**
62759	**N-Nitrosodimethylamine**	**100**
684935	**N-Nitroso-N-methylurea**	**1000**
56382	**Parathion**	**10**
75445	Phosgene	10
7803512	**Phosphine**	**10**
7723140	**Phosphorous**	**10**
75558	1,2-Propylenimine (2-Methyl aziridine)	100
1746016	2,3,7,8-Tetrachlorodibenzo-p-dioxin	100,000
8001352	**Toxaphene (Chlorinated camphene)**	**100**
75014	Vinyl chloride	10

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[a] Pollutants in boldface were added to this list.

[b] Weighting factor was adjusted from 10 to 100.

program." (56 FR 27356-27357) The preferable method of developing this general emission reduction plan would be a site- and source-specific evaluation of control technology feasibility, performance, and cost. This special provision is expected to be available to the following source categories.

- SOCMI (sources subject to the HON)
- coke ovens
- dry cleaners using perchloroethylene and 1,1,1-trichloroethane
- commercial sterilizers
- chromium electroplating and chromic acid anodizing cooling towers
- halogenated solvent cleaners

Since a number of these standards (the HON, coke ovens, and perchloroethylene dry cleaners) have been proposed, the opportunity for early reductions submittals no longer exists for these sources. Sources in the remaining categories have only limited time to conduct early reductions planning and apply to participate in the program. Final regulations governing compliance extensions for early reductions of emissions were promulgated on December 29, 1992 (57 FR 61970) [*15*]. The most significant change from the proposed regulations was the modification of the list and weighting of high-risk pollutants. These changes resulted from a change in selection methodology, deletion of pollutants because of new health effects data, and increased weighting factors to account for bioaccumulation or persistence of the pollutants. The final list of high-risk pollutants is given in Table 4. As of December 9, 1992 (57 FR 58203) [*9*], 12 applications for early reductions were considered complete by EPA. By February 1993, EPA had received a total of 85 early reduction submittals.

PREPARATION OF PERMIT APPLICATIONS

The operating permit program regulations (40 CFR Part 70) proposed in response to Title V of the CAA do not specify unique requirements for permit applications involving MACT standards. All sources subject to Section 112 of the Act are required to apply for a permit under the Title V program, regardless of whether the source is subject to an existing NESHAP or to future standards requiring MACT or addressing unreasonable residual risks. The criteria that define a complete application are to be established by the various state programs. The federal regulations set minimum requirements for a permit application that include an "identification and description of air pollution control equipment". The preamble to these regulations notes that the description is to be detailed, but does not elaborate. Presumably, a description of the key design and operating parameters for the type of control equipment will be adequate, while vendor-specific information would be appropriate if it is available. A source-specific evaluation of the emission reduction techniques that would be capable of achieving the emission standard with the most cost effective combination of feasible control and pollution prevention techniques would be advisable for sources subject to MACT. This type of evaluation is particularly advisable for the SOCMI where a large number of emission sources may require control, opportunities may exist for pollution prevention and emission averaging, and a number of alternative techniques may be capable of achieving the MACT emission standard.

DETERMINATION OF BEST TECHNOLOGY AND PRACTICE

If EPA fails to issue a standard for a category or subcategory of emission sources within 18 months of a scheduled promulgation date, the permitting authority (stage agency of EPA) must develop and enforce MACT on a case-by-case basis in accordance with Section 112(j) of the CAA (as amended). In the event that a MACT standard is not issued within the specified time, any major source (i.e., any group of sources emitting 10 tons/year of any one HAP or 25 tons/year of any combination of HAPs) is required to submit a permit application. The permitting authority is required to impose permit limitations equivalent to the limitation that the emission standard would have applied to that particular emission source. Obviously this determination of best technology and practice by a state agency (unless the state has not been delegated permitting authority) would have to parallel a MACT determination by EPA. If required, these case-by-case determinations could consume significant portions of a state's resources, especially if a nearly completed EPA regulatory development document is not available.

In addition, under Section 112(g) a MACT determination must also be made for major sources of HAPs that construct, reconstruct, or modify before the promulgation of applicable MACT standards, as well as for major sources that modify after the promulgation of applicable standards. The emission threshold levels that will define a modification and possible toxicity rankings for determination of offsets have not yet been defined. EPA is currently developing a guidance manual for making MACT determinations under Sections 112(g) and 112(j). As planned, this manual will address the following topics:

- emission sources that require MACT determinations;
- control technologies that meet the "MACT floor" requirement;
- data bases providing for technology transfer; and
- administrative procedures for making a MACT determination.

A draft of the MACT guidance manual has been prepared and is being internally reviewed by EPA.

ASSESSMENT OF RESIDUAL RISK

Within six years after the enactment of the CAAA, EPA is to prepare a report to Congress assessing the public health risk of residual air toxic emissions after implementation of the MACT standards and recommending legislation to address that remaining risk. If Congress does not pass such legislation EPA is to promulgate any standards necessary to "provide an ample margin of safety to protect public health" within eight years of the promulgation of MACT standards for the source category. These standards are to be based on risk rather than technology or cost. However, a more stringent standard than that necessary to provide an ample margin of safety may not be promulgated to prevent an adverse environmental effect without "taking into consideration costs, energy, safety and other relevant factors".

As part of the risk assessment activities required by Title III of the CAAA, the National Academy of Sciences is reviewing the methodology of EPA uses to assess the carcinogenic risk associated with exposure to HAPs. This study is evaluating the entire process from estimating carcinogenic potency to exposure estimation.

PREVENTION AND MITIGATION OF ACCIDENTAL RELEASES

The CAAA also require EPA to establish chemical accident prevention and mitigation regulations. On January 19, 1993 (58 FR 5102), EPA proposed a list of substances with threshold values that would be covered by the accidental release prevention regulations. This list includes 100 toxic substances, 62 flammable substances (gases and volatile liquids), and commercial explosives classified by the Department of Transportation as Division 1.1. Threshold quantities for applicability range from 500 to 10,000 pounds for toxics, 10,000 pounds for flammables, and 5,000 pounds for explosives. Risk management plan requirements have not been proposed.

SUMMARY

This paper has outlined the basic requirements and structure of the HAP programs under the Clean Air Act Amendments for 1990. An update of the major regulator activities has been provided as of February 1993. The statue of MACT determinations, the early reductions program, relevant operating permit program requirements, best technology and practice determination, residual risk evaluations, and accidental release regulations have been summarized.

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Measurement of Gas-Liquid Mass Transfer Coefficients for Volatile Organic Compounds in Sewers

Arlene Whitmore
School of Engineering, University of Guelph, Guelph, Ontario N1G 2W1

Richard L. Corsi
Department of Civil Engineering, The University of Texas, Austin, Texas 78712

Field experiments were completed to determine gas-liquid mass transfer coefficients for VOCs in sewers characterized by uniform flow conditions. Both deuterated chloroform and 1,1,1-trichloroethane were used as surrogate volatile tracers during four experiments in two operating sanitary sewers. Experimental mass transfer coefficients were in good agreement with those predicted using a diffusivity-adjusted oxygen transfer model. The experimental methodology provides a protocol for future studies of VOC mass transfer in municipal and on-site industrial sewers.

INTRODUCTION

Volatile organic compounds (VOCs) are discharged to municipal and on-site industrial sewers from a large number of sources. Concerns regarding the occurrence of VOCs in wastewater include their potential inhibitory effects on downstream biological treatment processes, and adverse ecological impacts on ultimate receiving systems. Recent studies have raised new concerns regarding airborne emissions of VOCs from wastewater. These concerns include:

1) Many VOCs are considered to be toxic air contaminants (TAC) that can pose inhalation exposure risks to treatment plant employees and the general public.
2) Many VOCs and semi-VOCs are considered to be reactive organic gases (ROGs) that contribute to the production of ozone in urban airsheds.
3) Some VOCs are relatively inert in the troposphere, e.g. 1,1,1-trichloroethane, but act in a similar manner to chlorofluorocarbons in depleting stratospheric ozone.
4) With sufficient gaseous accumulation in sewers, many VOCs pose explosion hazards.

The validity of the latter concern has been well documented following several tragic historical events. However, the significance of municipal wastewater as a source of TAC and ROG emissions has not been determined, and past studies have focused on the fate of VOCs during wastewater treatment, as opposed to wastewater collection. An improved understanding of the transfer of VOCs between wastewater and overlying confined atmospheres is important for assessing the relative significance of sewers as sources of VOC emissions. Such knowledge should also prove valuable in the development of municipal sewer use by-laws.

In this paper, a research effort focused on determining gas-liquid mass transfer of VOCs along uniform sewer reaches is described. Specific research objectives were: 1) to design and conduct field experiments that would yield overall mass transfer coefficients in two distinctly different sewer reaches, and 2) to evaluate a mass transfer coefficient model based on data obtained from existing literature coupled with data obtained through the aforementioned experiments.

BACKGROUND

Over the past ten years, close attention has been paid to aqueous discharges and gaseous emissions of VOCs from municipal and industrial wastewater treatment facilities [*1*, *2*, *3*, *4*, *5*, *6*]. Recent studies have also recognized the potential for VOC emissions from sewers [*7*, *8*]. Evidence of the occurrence and levels of VOCs in municipal sewers has been provided by monitoring events carried out at numerous locations [*8*, *9*, *10*, *11*].

Municipal and on-site industrial sewers can be thought of as reactors within which the fate of VOCs is determined by the simultaneous action of several biological, chemical and physical reactions, or transfer mechanisms. Biodegradation/transformation of VOCs can occur due to biomass suspended in wastewater or biologically active slime layers attached to wetted sewer walls. Chemical reactions are likely to be small for most VOCs in sewers. However, waste chlorine discharges or addition of chlorine to sewers for hydrogen sulfide control may lead to some trihalomethane formation [*12*]. Physical transfer mechanisms can include adsorption to solid particles, absorption within immiscible liquids, and mass transfer between wastewater and an overlying sewer atmosphere. The latter is the focus of this study. Its relative impact on the fate of VOCs in sewers is complicated by air exchange between sewer and ambient atmospheres. Such exchange can occur through a large number of openings in most sewer systems, e.g., manhole covers, building connections/risers, industrial process drains.

Mass transfer across a gas-liquid interface is often expressed as:

$$R_v = K_L \left\{ C_l - \frac{C_g}{H_c} \right\} A \qquad (1)$$

where,

R_v = rate of mass transfer across interface, M/T
K_L = overall mass-transfer coefficient, L/T
A = interfacial area, L^2
C_l = mass concentration dissolved in liquid-phase, M/L^3
C_g = mass concentration in gas-phase, M/L^3
H_c = Henry's law constant, $(M/L^3)_{\text{gas}}/(M/L^3)_{\text{liquid}}$.

In accordance with two-film theory [13], the overall mass transfer coefficient may be expressed as:

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_g H_c} \qquad (2)$$

where,

k_l = liquid-phase mass transfer coefficient, L/T
k_g = gas-phase mass transfer coefficient, L/T.

The terms $1/k_l$ and $1/k_g H_c$ are commonly referred to as liquid and gas-phase resistances to mass-transfer, respectively.

The second term on the right hand side of equation (2) becomes small relative to $1/k_l$ when the product $k_g H_c \gg k_l$. For many systems k_g/k_l has been reported to be greater than 100 [14]. In such cases, liquid-phase resistance represents greater than 90 percent of the overall resistance to mass transfer for compounds with $H_c > 0.1$. However, lower values of k_g/k_l have been reported for some systems. For example, values of k_g/k_l have been reported to range from 20 to 60 [15] and from 38 to 110 [16] for mechanical surface aeration, and to be as low as 2.2 to 3.6 [17] for diffused-bubble aeration. With k_g/k_l equal to 20, liquid-phase resistance accounts for greater than 90 percent of total resistance to mass transfer for compounds with $H_c > 0.5$ $[\text{mg/m}^3]_{\text{gas}}/[\text{mg/m}^3]_{\text{liq}}$.

Of all the variables presented in equations (1) and (2), the mass transfer coefficients, K_L, k_l and k_g remain the most difficult to routinely quantify. As noted above, for VOCs with high H_c, concern rests primarily in obtaining a value for k_l. Although theoretical factors affected should be affecting liquid-phase mass transfer coefficients, such as surface renewal rate or hypothetical film thicknesses, have been suggested, the means to determine their effect in real systems generally does not exist. For this reason, models used to estimate gas-liquid mass transfer coefficients are empirical or semi-empirical at best, with most having been developed to predict oxygen mass transfer coefficients for clean water flowing in natural or engineered open channels [18, 19, 20].

Parkhurst and Pomeroy [21] developed the only reported model for mass transfer within sewer environments. According to their semi-empirical model:

$$K_{Lo} = 2.67 \times 10^{-4}(1 + 0.17F^2)\gamma(US)^{3/8} \qquad (3)$$

where,

K_{Lo} = overall mass transfer coefficient for oxygen, m/s
F = Froude number = $U/[gd]^{1/2}$,
g = gravitational acceleration = 9.8 m/s^2
d = depth of flow, m
γ = temperature correction factor,
S = slope of the energy gradient, m/m
U = wastewater mean velocity, m/s.

For gases with high Henry's law constants, such as oxygen, the gas film offers relatively little resistance to mass transfer. Therefore, the overall mass transfer coefficient for oxygen is approximately equal to its liquid-phase mass transfer coefficient.

Predictions of oxygen mass transfer coefficients allow subsequent estimation of liquid-phase mass transfer coefficients for other compounds using the relationship:

$$\Psi = \frac{k_{li}}{K_{Lo}} = \left\{ \frac{D_{li}}{D_{lo}} \right\}^n \qquad (4)$$

where,

Ψ = ratio of VOC-to-oxygen liquid-phase mass transfer coefficients,
D_{li} = liquid molecular diffusion coefficient for compound i, L^2/T
D_{lo} = liquid molecular diffusion coefficient for oxygen, L^2/T
k_{li} = liquid-phase mass transfer coefficient for compound i, L/T
K_{Lo} = overall mass transfer coefficient for oxygen, L/T
n = exponent which varies depending on the degree of liquid agitation.

The value of n varies from 0.5 to 1.0 according to penetration [22] and two-film [13] theories, respectively. Even when a value of n is not known for a given system, it has been shown that for compounds with $H_c > 0.1$, Ψ generally ranges from 0.5 to 0.7 in natural surface waters and wastewater [23, 24].

Other than Parkhurst and Pomeroy [21], only a few researchers have investigated gas-liquid mass transfer along uniform sewer reaches. Jensen and Hvitved-Jacobsen [25] developed a method for measuring oxygen mass transfer coefficients in a 2.3 km gravity-flow sewer reach (0.6–0.7 m diameter) in Aalborg, Denmark. It involved the use of krypton-85 as a gaseous radio-tracer, and tritium as a non-gaseous indicator of dispersion. A value of Ψ for krypton and oxygen had been determined in a previous study by Tsivoglou et al. [26]. This was coupled with equation (3) to yield predicted mass transfer coefficients that were reported to be approximately 21 percent greater than experimentally determined transfer coefficients over three experiments.

Corsi *et al.* [7] reported the results of four mass transfer experiments completed in two different reaches in California. Deuterated chloroform was used as a volatile tracer. Mass transfer coefficients that were predicted by combining equations (3) and (4) were reported to be within +/− 33 percent of experimentally determined mass transfer coefficients.

EXPERIMENTAL METHODOLOGY

Four field experiments were completed in two operating gravity-flow sewer reaches in the City of Guelph. Each experiment was designed to facilitate the determination of K_L using surrogate volatile tracers. Experimental K_L were then used for comparison with values predicted using equations (3) and (4), with required model variables being consistent with conditions observed during each experiment. Pipe diameters for Guelph Experimental Reach #1 (Guelph #1) and Guelph Experimental Reach #2 (Guelph #2) were 1.2 m and 0.52 m, respectively. Channel slopes were 0.10 percent (Guelph #1) and 3.5 percent (Guelph #2). The section of each reach that was used for tracer experiments was 122 m for Guelph #1 and 64 m for Guelph #2. Wastewater that was transported along

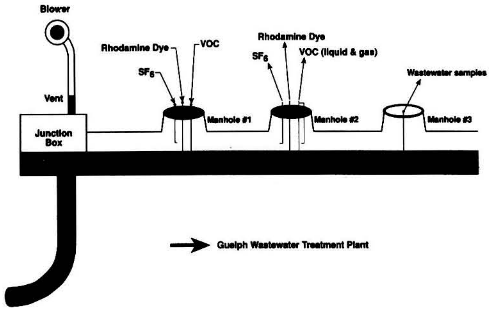

FIGURE 1. Experimental arrangement for Guelph reach #1.

Guelph #1 represented a mix of residential, commercial and light industrial discharges. Wastewater conveyed along Guelph #2 was primarily residential. The channel slope for Guelph #2 represented an extreme condition within the City of Guelph. The experimental systems are illustrated in Figures 1 and 2. Major components of each system are described below.

Headspace Ventilation

Experimental reaches were force-ventilated using a small blower powered by a portable generator. This provided constant ventilation throughout the duration of an experiment, and also accelerated the rate at which steady-state conditions were achieved. Two different blowers were used depending on the desired ventilation rate. Wooden plates (22.5 cm diameter) were sealed around the outlets of each blower. This allowed the blowers to be interchangeably mounted on a sheet metal stack 22.5 cm in diameter and 61 cm in length. This stack provided an outer shell that could be slipped over the 22.5 cm diameter vent on a junction box (Guelph #1), or mounted on Manhole #1 (Guelph #2).

Upstream transport of forced-air was not possible on Guelph #1, as the junction box received wastewater from an inverted siphon which effectively formed a gas seal. To minimize upstream gas flow on Guelph #2, an neoprene skirt was inserted in the headspace immediately upstream of Manhole #1, allowing only a small air gap between the sewer headspace and wastewater surface. Furthermore, the blower at Manhole #1 was modified to include a section of dryer hose which formed a 90° bend immediately above the wastewater surface, i.e., blowing air in the downstream direction.

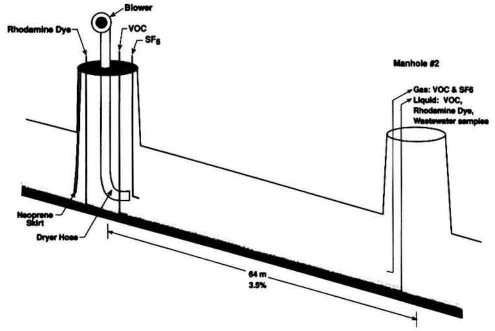

FIGURE 2. Experimental arrangement for Guelph reach #2.

Headspace ventilation rates were confirmed by dilution of an inert tracer, sulfur hexafluoride. A 40 L Tedlar® bag was filled with SF_6 (99.8 percent purity) and transported to the field. An air sample pump (SKC model 224-PCXR7), a single-port manifold, and 6. 5 mm o.d. polyethelene tubing was used to inject SF_6 into the headspace of the sewer reach, approximately 6 cm above the surface of the wastewater at Manhole #1. The system was allowed to reach steady-state by waiting a minimum of three aerodynamic residence times prior to collecting samples. An air sample pump and 6.5 mm o.d. polyethylene tubing were then used to draw headspace gas, at a rate of 2.5 L per minute at Manhole #2. A plastic T-connection within the line allowed the collection of five gas samples using sterile 10 mL plastic surgical syringes with PVC Luer-lok stopcocks.

Analyses of gaseous SF_6 samples were completed using a gas chromatograph (Hewlett-Packard 5890 Series II with a J&W Scientific #123-5033 30 m DB-5 capillary column) equipped with an electron capture detector (GC/ECD). All gas samples were analyzed by drawing 10 μL of air from each sample syringe followed by direct injection into the GC column. Three-point calibration curves were developed by direct-injection of standards prepared by sequential dilution of a gaseous SF_6 stock standard mixed with ultra-high purity (UHP) nitrogen. Sulfur hexafluoride concentrations in all gaseous field samples fell within the range defined by calibration curves, 0.33 to 0.66 mg/L.

Wastewater Flow Characteristics

The dilution of an inert tracer dye was selected as a practical means of determining sewer reach hydrodynamics and wastewater flow rates. Before beginning each experiment, two wastewater blanks were collected. During the hydrodynamic portion of the test, rhodamine dye (10.3 g/L) was pumped directly into wastewater below Manhole #1 at a rate of 180 mL/min for 2 minutes. Forty wastewater samples were then collected at Manhole #2. During each experiment, the sewer channel approached ideal plug-flow behavior with little axial dispersion.

A second batch of rhodamine dye (5.2 g/L) was pumped into the wastewater below Manhole #1 at a rate of 50 mL/min for 30 minutes to determine wastewater flow rate by dilution. Again, samples were collected at Manhole #2. Polyethylene tubing (6.5 mm o.d.) and a peristaltic pump (Cole-Parmer 6–600 rpm) were used for both injection and collection.

A spectrofluorometer (Turner Model 430) was used to complete rhodamine dye analyses. Four-point linear calibration curves were developed by sequential dilution of a 10 mg/L stock rhodamine dye standard. Wastewater blanks collected at the beginning of each experiment were used to judge the baseline fluoroscence of wastewater prior to the addition of rhodamine dye. Rhodamine dye concentrations in all liquid field samples fell within the range defined by calibration curves, 21 to 515 μg/L.

Wastewater and Headspace Fluid Characteristics

Wastewater and headspace temperatures and dissolved oxygen concentrations were measured directly using an on-line temperature/dissolved oxygen probe (YSI model #5740) and meter (YSI model #58) at Manhole #3 (Guelph #1) or Manhole #2 (Guelph #2). Over all experiments, wastewater temperature varied from 16°C to 19°C, sewer gas temperature varied from 18°C to 23°C, and wastewater dissolved oxygen concentrations varied from 0.2 mg/L to 4.7 mg/L.

Wastewater samples were collected at Manhole #3 (Guelph #1) or Manhole #2 (Guelph #2) using either a "dipping" cup or peristaltic pump, respectively. Those samples were used to quantify wastewater conductivity and pH in the field using

Table 1 Physicochemical Properties of Experimental Tracer Compounds

Compound	Molecular Weight	Solubility@25°C, mg/L	$\text{Log}_{10}(K_{ow})$	H_c@20°C (mg/L)·gas/(mg/L)·liq
$CDCl_3$	120.4	7950	1.97	0.12
TCA	133.4	1495	2.49	0.60

$\text{Log}_{10}(K_{ow})$ from reference [28]; H_c based on reference [29].

portable meters (conductivity—Hanna Instruments HI#8033; pH—Cole Parmer Chem Cadet model #5850-00). Wastewater samples were also returned to the laboratory for analysis of total suspended solids (TSS) using Standard Method 2540 D [27]. Over all experiments, the conductivity of wastewater varied from 1460 to 1580 micromhos, pH varied from 7.8 to 9.3, and TSS varied from 98 mg/L to 293 mg/L.

Volatile Tracers

Two volatile organic compounds, deuterated chloroform ($CDCl_3$, 99.8 percent atom D) and 1,1,1-trichloroethane (TCA, 96.5 percent), were used as tracers during each field experiment. These compounds were selected as tracers on the basis of: differences in their Henry's law constants, ability to dissolve to high concentrations in water prior to injection into wastewater, lack of detection in background samples collected in the experimental reaches during preliminary site investigations, and relatively low octanol-water partition coefficients (K_{ow}) and associated low affinities for adsorption to suspended solids. The latter is particularly true for the range of TSS concentrations observed over all four field experiments, as described above. The use of dual tracers, as opposed to the single compound experiments reported previously [7, 25, 26], also allowed for confirmation of experimental mass transfer coefficients. The physicochemical properties of each tracer are listed in Table 1.

In preparing for each experiment, a 40 L Tedlar® bag was filled with 23.8 L of tap water using a peristaltic pump and 6.5 mm o.d. polyethylene tubing. A 200 mL methanol solution containing the selected tracers was then pumped into the bag using a peristaltic pump and FEP Teflon® tubing. Twelve hours were allowed between bag filling and experiments in order to ensure that complete dissolution of both tracer compounds had taken place. Consideration of all experimental factors meant that different solution concentrations and/or injection rates were employed for each experiment. Over the course of the four experiments, target solution concentrations ranged from 312 to 625 mg/L for deuterated chloroform and from 279 to 558 mg/L for 1,1,1-trichloroethane.

During each experiment, the tracer solution was pumped from the Tedlar® bag into wastewater at Manhole #1 using 6.5 mm o.d. FEP Teflon® tubing and a peristaltic pump calibrated to deliver a specific flow rate dependent upon experimental conditions. The Tedlar® bag collapsed as it was evacuated, ensuring that no headspace developed during the injection period.

A minimum of three hydraulic and aerodynamic residence times were allowed prior to sample collection in order to assure steady-state conditions. Subsequent observations verified that neither gas nor liquid sample concentrations increased during the course of experimental sampling. Once this time had been reached in the field, both gas and liquid samples were collected at Manhole #2. Wastewater was pumped to the surface using 6.5 mm o.d. FEP Teflon® tubing and a peristaltic pump. Four liquid samples were collected in 40 mL amber/borosilicate vials capped with 3 mm Teflon® fluorocarbon resin silicone septa (Precleaned to EPA Protocol B Cleaning Standards). Collection was accomplished with as little agitation as possible and no headspace was permitted in the capped vials. All liquid samples were immediately stored in an ice chest.

Sewer gas was pumped to the surface using 6.5 mm o.d. FEP Teflon® tubing and an air sample pump equipped with a single port manifold. Five gas samples were collected on 6.5 mm o.d. stainless steel sorbent tubes (Carbotrap™ 300 multi-bed thermal desorption tubes) sequentially packed with two graphitized carbon black adsorbent beds (Carbotrap C and Carbotrap), and a spherical carbon molecular sieve (Carbosieve™). Twelve hours prior to each experiment, all tubes were thermally conditioned at 280°C for 3 hours. Following gas collection, each tube was sealed using Teflon® ferrules and stainless steel Swagelok® plugs at both ends. All gas samples were immediately stored in a hermetically-sealed glass container and kept in an ice chest. Upon return to the laboratory, VOC samples were transferred to a refrigerator and maintained at 4°C.

Prior to sample analysis, each liquid sample was concentrated onto a clean Carbotrap™ 300 adsorbent tube by sparging with charcoal-polished UHP nitrogen gas at 100 mL/min for 10 minutes. All concentrated liquid and gas samples were analyzed using the following method: thermal desorption by replacement of the internal focussing trap of a Tekmar LSC 2000 purge and trap unit (dry purge for 2.50 minutes with charcoal-polished UHP helium, desorption at 190°C for 2.75 minutes, bake at 260°C for 2.00 minutes); transfer to a Hewlett-Packard 5890 Series II GC oven equipped with a J&W Scientific DB-5 30 m×0.20 mm i.d. capillary column with 1.0 μm film thickness (desorbed analytes condensed at the column head at 25°C, oven ramp at 30°C/min to 39°C, hold for 2.20 minutes, ramp at 9°C/min to 150°C, ramp at 30°C/min to 210°C, hold for 2.00 minutes); transfer to a Hewlett-Packard model 5971 mass selective detector (MS) set to scan all ions from m/e 25 to m/e 250 at approximately 2 cycles/s. External calibration curves were generated using a stock solution of $CDCl_3$ and TCA. A minimum of four-point external calibration curves were prepared for each experiment. All experimental samples fell within the mass range defined by calibration curves, generally 40 to 800 ng.

Determination of Mass Transfer Coefficients

Overall mass transfer coefficients were determined by solving equation (1) for K_L such that:

$$K_L = \frac{R_v}{\left\{C_l - \frac{C_g}{H_c}\right\} A}. \tag{5}$$

For short reaches of sewer, e.g., reach lengths used in this study, the reduction in concentration of a VOC dissolved in wastewater is generally much less than analytical (GC/MS) accuracy. However, for steady-state conditions the accumulation of volatile tracers in the headspace of the experimental systems was sufficient to easily quantify gas-phase concentrations. Thus, integrated emissions along the experimental reaches were determined by:

Table 2 Flow Conditions and Concentrations of Tracers in Wastewater and Sewer Gas

	Wastewater		Sewer Gas		Concentration (mg/m^3)			
					$CDCl_3$		TCA	
Experiment	Flow Rate m^3/s	Velocity m/s	Flow Rate m^3/min	Velocity m/s	liquid	gas	liquid	gas
1.1	0.17	0.72	2.5	0.044	18	0.38	8.4	0.20
1.2	0.071	0.56	2.1	0.035	13	0.25	5.0	0.06
1.3	0.10	0.62	11	0.18	49	0.15	42	0.23
2.1	0.020	1.5	1.8	0.15	94	2.3	99	2.8

$$R_v = Q_g C_g \tag{6}$$

where,

R_v = net rate of mass transfer across the gas-liquid interface, M/T
Q_g = gas flow rate in sewer headspace, L^3/T
C_g = tracer concentration in gas phase at Manhole #2, M/L^3.

The concentration in wastewater (C_l, M/L^3) was measured from liquid samples collected at Manhole #2 in each reach. Henry's law constants for $CDCl_3$ and TCA were estimated using wastewater temperatures according to Gossett [*29*]. No perturbations of interfacial surface area were observed during any of the four field experiments. Thus, surface area (A) was determined as the product of reach length and surface width, where surface width was estimated by geometric considerations using pipe diameter and depth of flow. For the four experiments described in this paper, surface width varied from 0.33 m (Guelph #2) to 1.0 m (Guelph #1), and surface area varied from 21 m^2 (Guelph #2) to 127 m^2 (Guelph #1).

The gas concentration required to determine the C_g/H_c term in equation (5) varied as a function of distance along each sewer reach. However, C_g/H_c was generally much less than C_l. For example, the magnitude of C_g/H_c for $CDCl_3$ was less than 25 percent of C_l for all experiments. Similarly, for TCA the magnitude of C_g/H_c was always less than 5 percent of C_l. Thus, an average value of C_g was used, i.e., 50 percent of the maximum value at the end of the reach. Based on the analyses described above, this approximation was determined to yield less than a 2 percent difference relative to values of K_L determined with either a maximum or minimum estimate of C_g for TCA. Similarly, the difference for $CDCl_3$ should not have been greater than 12 percent relative to values of K_L determined with either a maximum or minimum estimate of C_g.

The approach described above was verified using a two-phase finite volume model described elsewhere [*7*]. Model inputs were consistent with conditions for each of the four experiments. Differences between iteratively back-calculated K_L values obtained using the model and those determined using equations (5) and (6) were always less than 7 percent, well within the experimental uncertainties described below.

Error Estimation

Errors associated with determination of experimental K_L for this study were estimated using an error propagation method based on differentiation of equations (5) and (6) with respect to each variable on the right-hand-side of equation (5):

$$\Delta K_L = \sum \frac{\partial K_L}{\partial X_i} \Delta X_i \tag{7}$$

where,

ΔK_L = overall uncertainty in K_L, M/T
X_i = variable i
ΔX_i = uncertainty in variable i.

Percent uncertainties associated with Q_v, C_g and C_l were assumed to be equal to the maximum coefficients of variation for each variable over all four experiments. Uncertainties in H_c were assumed to be +/− 15 percent based on maximum differences reported in the literature for consistent temperatures. An uncertainty of 20 percent for A was based on maximum coefficients of variation in replicate rhodamine dye samples which were used to determine wastewater flow rates. The signs associated with ΔX_i were selected to maximize estimates of uncertainty, i.e., error estimates for K_L were determined as worst-case.

Sufficient data were not available to estimate uncertainties in mass transfer coefficients determined from previous studies in Denmark [*25*] and California [*7*].

RESULTS AND DISCUSSION

Table 2 provides a summary of wastewater and gas flow conditions for Guelph #1 (Experiments 1.1-1.3) and Guelph #2 (Experiment 2.1). The gas flow rates listed in Table 2 may be translated into ventilation rates expressed as number of turnovers per day (TuPD). By convention, these turnovers are based on empty pipe volume. Ventilation rates for Experiments 1.1 through 2.1 varied from 22 to 190 TuPD. These ventilation rates were one to two orders of magnitude higher than estimates

Table 3 Reach Operating Characteristics for this Study and Other Reported Experiments

Characteristic	Guelph #1	Guelph #2	Aalborg[a]	Davis[b]	Sacramento[b]
Diameter, m	1.2	0.52	0.6–0.7	0.5	2.6
Slope, %	0.10	3.5	0.09	0.24	0.063
Wastewater Flow, m^3/s	0.071–0.17	0.020	0.018–0.021	0.03–0.06	2.1–2.6
Gas Flow, m^3/s	0.035–0.18	0.030	[c]	0.02–0.03	1.8
Length, m	122	64	2310	131	291

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[a] Reference [*25*]
[b] Reference [*7*]
[c] The Aalborg reach was not force-ventilated, and natural ventilation rates were not reported.

of natural ventilation rates reported by Pescod and Price [30]. They reported that ventilation rates required to maintain the 85 percent of normal oxygen levels typical in 1.50 m and 0.45 m diameter sewer pipe atmospheres ranged from 0.51 to 2.34 TuPD, respectively. However, Quigley et al. [31] reported measured ventilation rates of as high as 19 TuPD in a municipal sewer interceptor in Toronto, Ontario.

Average gas and liquid-phase concentrations of each volatile tracer are also presented in Table 2. In the case of gas samples, a time-weighted average (TWA) was used to reflect different lengths of time over which gas samples were collected. Overall, liquid samples exhibited lower variances than gas samples. Coefficients of variation for liquid samples ranged from 1.7 percent to 24 percent, while coefficients of variation for gas samples ranged from 8.9 percent to 43 percent.

Sewer operating characteristics are listed in Table 3 for the Guelph experiments as well as experiments completed by Corsi et al. [7] and Jensen and Hvitved-Jacobsen [25]. The pipe diameter, slope, wastewater flow rates, and gas flow rates associated with Guelph #1 fell within the range defined by the two California reaches studied by Corsi et al. [7]. Guelph #2, however, was significantly different than the other reaches in terms of its large channel slope and wastewater velocity, with corresponding high degree of turbulent mixing of the wastewater.

Experimental Mass Transfer Coefficients

Experimental mass transfer coefficients (K_L) are listed in Table 4 for the four experiments described in this paper, along with those reported for Davis, Sacramento, and Aalborg [7, 25]. Uncertainty estimates for the experiments described in this paper are also provided in Table 4. Experimentally determined K_L were generally estimated to be accurate to within a factor of two. Insufficient information was available to estimate the uncertainties for the California and Aalborg experiments. Additionally, for the Aalborg experiments there was insufficient data provided to estimate K_L. Thus, only the K_La values reported by the authors are listed in Table 4.

Over all experiments, mass transfer coefficients varied by a factor of 11, from a low of 0.014 m/hr (Guelph #1; TCA-Expt. 1.1) to a high of 0.15 m/hr (Guelph #2; TCA). Mass transfer coefficients generally increased in the order of Guelph #1, Sacramento, Davis and Guelph #2. The latter should approach a maximum for municipal sewers, as Guelph #2 was characterized by both a large channel slope (3.5 percent) and high wastewater mean velocity (1.5 m/s). These results suggest that K_L can vary significantly from reach-to-reach, and that application of reach-independent mass transfer coefficients to predict gas-liquid mass transfer of VOCs in sewers may lead to significant error.

For the two Guelph reaches, there were no apparent differences in K_L between $CDCl_3$ and TCA. For two of the experiments (Expt. 1.1 and Expt. 2.1) K_L values for $CDCl_3$ and TCA were essentially equivalent. Values of K_L for $CDCl_3$ were approximately factors of 2.0 greater and less than K_L for TCA during Experiments 1.2 and 1.3, respectively. For the experimental conditions, values of H_c for TCA were approximately a factor of five greater than H_c for $CDCl_3$. Therefore, if k_g is not much greater than k_l in equation (2), K_L for $CDCl_3$ should have been observed to be lower than K_L for TCA. Since this did not appear to be the case, it is likely that k_g was much greater than k_l and gas-phase resistance to mass transfer was small for the four Guelph experiments.

The results listed in Table 4 suggest that the experimental protocol outlined in this paper should allow determination of reach-specific mass transfer coefficients to within a factor of two or better. Furthermore, the use of dual tracers should prove valuable for confirmation of VOC mass transfer coefficients or the determination of both liquid and gas-phase mass transfer coefficients. The latter would require one volatile tracer, e.g., $H_c > 0.1$ $[mg/m^3]_{gas}/[mg/m^3]_{liq}$, for which gas-phase resistance to mass transfer is small, and one tracer with a relatively low value of H_c, e.g., $\ll 0.1$ $[mg/m^3]_{gas}/[mg/m^3]_{liq}$, for which gas-phase resistance to mass transfer is significant.

Effects of Potential Energy Dissipation

As noted above, overall mass transfer coefficients generally increased in the order of Guelph #1, Sacramento, Davis and Guelph #2. This was also the order of increasing US, where U is wastewater mean velocity and S is the slope of the energy gradient. The value of S is equal to channel slope for uniform flow conditions. Conceptually, US is the rate of potential en-

Table 4 Experimental and Predicted Mass Transfer Coefficients

Site	Compound	Mass Transfer Coefficient, m/h Experimental	Predicted	Expt. Uncertainty (factor of)
Guelph #1				
Expt 1.1	$CDCl_3$	0.027	0.029-0.041	2.2
	TCA	0.029	0.026-0.039	2.1
Expt 1.2	$CDCl_3$	0.024	0.027-0.039	2.3
	TCA	0.014	0.023-0.035	2.0
Expt 1.3	$CDCl_3$	0.018	0.028-0.040	2.1
	TCA	0.032	0.025-0.038	2.1
Guelph #2				
Expt 2.1	$CDCl_3$	0.14	0.29-0.42	2.1
	TCA	0.15	0.28-0.42	2.0
Davis				
Test 1	$CDCl_3$	0.039	0.049-0.069	NA
Test 2	$CDCl_3$	0.071	0.049-0.069	NA
Test 3	$CDCl_3$	0.048	0.040-0.058	NA
Sacramento	$CDCl_3$	0.041	0.036-0.052	NA
Aalborg	Krypton	0.42/h[a]	0.36/h[a]	NA

[a] Aalborg transfer coefficients reported as K_La ($a = A/V$); A = total surface area and V = total system volume. Flow data were not provided to allow calculation of K_L.

NA. Insufficient data available to estimate experimental uncertainties in K_L.

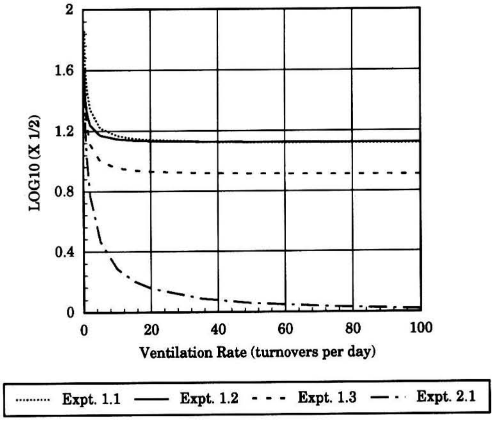

FIGURE 3. Effects of potential energy dissipation on experimental mass transfer coefficients.

ergy dissipation of a liquid flowing in an open channel. The rate of potential energy dissipation should be proportional to production of turbulent kinetic energy and associated turbulent mixing within the liquid stream. According to penetration theory [22], the mass transfer coefficient of a compound should be directly proportional to the degree of turbulent mixing as measured by surface renewal rate.

To estimate K_{Lo} for oxygen in natural streams, several models have been developed of the form:

$$K_{Lo} = b(US)^m \tag{8}$$

where,

b = empirical constant,
m = empirical or semi-empirical power constant.

Several models of the form described by equation (8) were reviewed by Frexes et al. [32]. They noted that values of m obtained by various investigators were in the range of 0.375 to 1, with most approximately 0.5. The lower-bound of this range is consistent with equation (3). A relationship similar to equation (8) can be used to model K_L for VOCs.

Taking $\log_{10}$ of each side of equation (8) applied to VOCs yields:

$$\log_{10}(K_L) = m\log_{10}(US) + \log_{10}(b) \tag{9}$$

or

$$-\log_{10}(K_L) = -m\log_{10}(US) - \log_{10}(b). \tag{10}$$

Thus, a plot of $-\log_{10}(K_L)$ versus $-\log_{10}(US)$ should allow an estimation of m and b through linear best-fit analysis.

As K_L is a function of temperature $[K_L(T)]$, analyses of experimental data should account for differences in liquid temperature between experiments. This is typically done by adjusting experimental $K_L(T)$ to a reference temperature, say 20°C $[K_L(20)]$, using an empirical adjustment factor θ such that:

$$K_L(20) = \frac{K_L(T)}{\theta^{T-20}}. \tag{11}$$

The value of θ is commonly accepted, as an ASCE standard, to be 1.024 for oxygen [33]. However, this value has also been applied to adjust mass transfer coefficients for other volatile chemicals such as krypton [25]. For this study, uncertainties associated with extrapolating $\theta = 1.024$ to chemicals other than oxygen were small, as wastewater temperatures were close to 20°C (16–19°C) over all four field experiments.

Values of b and m were obtained for the combined data set associated with Guelph #1, Guelph #2, Sacramento, and Davis using equations (10) and (11). A plot of $-\log_{10}[K_L(20)]$ versus $-\log_{10}(US)$ for the combined data set is provided in Figure 3. The data exhibited a clear trend of increasing K_L with increasing rate of potential energy dissipation. A least-squares best-fit equation using all data lead to values of $m = 0.40$ and $b = 0.52$. The resulting R^2 was 0.86. The power constant m was within the range of values reported previously for oxygen transfer to natural streams, and was close to the value used in equation (3).

The predicted b value (b_{pred}) using equation (3), converted to units of m/h, and equation (4) is:

$$b_{\text{pred}} = 0.96\Psi(1 + 0.17F^2). \tag{12}$$

The term $(1 + 0.17F^2)$ is intended to account for increases in surface area due to surface disturbances as Froude number (F) increases. For the four Guelph experiments, F ranged from 0.48 to 0.49 for Guelph #1, and was equal to 2.3 for Guelph #2. The associated values of $(1 + 0.17F^2)$ were 1.039 and 1.041 for Guelph #1, and 1.89 for Guelph #2. Use of $n = 1.0$ and $n = 0.5$ in equation (4) lead to Ψ estimates of 0.48 and 0.69, respectively, for $CDCl_3$. Similarly, Ψ estimates were 0.43 and 0.65 for TCA. Thus, for Guelph #1, b_{pred} ranged from 0.48 to 0.69 for $CDCl_3$ and from 0.43 to 0.65 for TCA. The experimental b of 0.52 was well within each of these ranges. For Guelph #2, b_{pred} ranged from 0.87 to 1.25 for $CDCl_3$, and from 0.78 to 1.18 for TCA. Thus, b_{pred} was greater than the best-fit experimental b by 34 percent to 127 percent. This was due to the large Froude number for Experiment 2.1, and subsequent increase in predicted surface area. However, as noted previously, visual observations during Experiment 2.1 (Guelph #2) suggested that surface disturbances were negligible at both Manhole #1 and Manhole #2.

Comparison with Predicted Mass Transfer Coefficients

Liquid-phase mass transfer coefficients (k_l) were estimated using equations (3) and (4), such that:

$$k_l = 2.67 \times 10^{-4}\left\{\frac{D_{li}}{D_{lo}}\right\}^n (1 + 0.17F^2)\gamma(US)^{3/8}. \tag{13}$$

Associated ranges of mass transfer coefficients predicted using $n = 0.5$ and $n = 1.0$ are listed in Table 4.

As noted previously, use of equation (3) with $\Psi = 0.83$ for krypton lead to a slightly lower $k_l a$ than the average $K_L a$ observed experimentally for Aalborg experiments. For Davis and Sacramento experiments, there was no apparent trend in differences between experimental K_L and predicted k_l. Two of the four experiments (Davis Test 3 and Sacramento) lead to K_L that were encompassed by corresponding ranges of k_l. Experimental K_L for Davis Tests 1 and 2 were 21 percent lower than the predicted lower-bound k_l and 3 percent greater than the predicted upper-bound k_l, respectively. It is likely that these differences were well within experimental error.

For the two Guelph sewer reaches, experimental K_L were less than predicted lower-bound k_l for six of eight experiments. On average, the ratio of K_L (experimental) to k_l (predicted lower-bound) was 0.81, and the ratio of K_L (experimental) to k_l (predicted upper-bound) was 0.55 over all eight experiments. Omitting Guelph #2, the ratio of K_L (experimental) to k_l (predicted lower-bound) was 0.92, and the ratio of K_L (experimental) to k_l (predicted upper-bound) was 0.62. As described

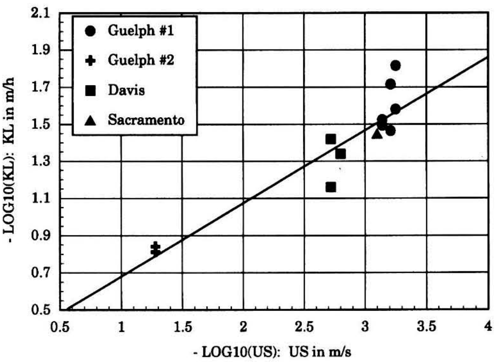

FIGURE 4. Predicted 1,1,1-trichloroethane half-length versus headspace ventilation rate for four reach experiments.

above, these differences can not be readily explained by gas-phase resistance to mass transfer. However, differences between K_L (experimental) and k_l (predicted upper-bound) were generally within estimated experimental uncertainty for Guelph #1, and differences between K_L (experimental) and k_l (predicted lower-bound) were within experimental uncertainties for Guelph #2. The most significant differences between K_L (experimental) and k_l (predicted) occurred for Guelph #2, in which case K_L (experimental) for both $CDCl_3$ and TCA were approximately a factor of two less than lower-bound k_l and three less than upper-bound k_l.

Based on the results of experiments completed on five sewer reaches, equations (3) and (4) provide reasonable first-estimates of K_L for VOCs in sewers, if gas-phase resistance to mass transfer is small ($k_g H_c \gg k_l$). Equations (3) and (4) appear to be less reliable for sewers with steep channel slopes, i.e., characterized by rapid dissipation of potential energy and associated production of turbulent mixing. For such conditions, the data reported in this study indicate that equations (3) and (4) may overestimate K_L by a factor of two or three. Depending on the specific application, this may warrant the experimental determination of reach-specific K_L using volatile tracers.

Stripping of VOCs along Sewer Reaches

Ultimately, knowledge of VOC mass transfer coefficients along sewer reaches can be used to estimate concentration reductions in wastewater as well as mass emission rates. Assuming that gas-liquid mass transfer is the dominant fate mechanism for VOCs in sewers, plug-flow conditions exist in both the gas and liquid phases, and sewer ventilation is uniformly distributed along a reach, the following two mass balance equations can be used to predict gas and liquid phase VOC concentrations along the reach:

$$\frac{\partial C_g}{\partial t} = -\frac{\partial U_g C_g}{\partial x} + K_L a\left(C_l - \frac{C_g}{H_c}\right)\frac{V_l}{V_g} - \frac{Q_{v\,\mathrm{out}}}{V_g}C_g + \frac{Q_{v\,\mathrm{in}}}{V_g}C_a \qquad (14)$$

and

$$\frac{\partial C_l}{\partial t} = -\frac{\partial U_l C_l}{\partial x} - K_L a\left(C_l - \frac{C_g}{H_c}\right) \qquad (15)$$

where,

C_a = ambient concentration of VOC, M/L^3
t = time, T
U_g, U_l = mean velocities in gas and liquid phases, respectively, L/T
x = spatial coordinate (or distance along sewer reach), L
a = specific surface area = A/V_l, $1/L$
$Q_{v\,\mathrm{in}}$, $Q_{v\,\mathrm{out}}$ = gas ventilation rates in and out of control volume, L^3/T
V_g, V_l = gas and liquid volumes, respectively, L^3.

A simplified analytical solution can be derived given the following additional assumptions:

1. $C_g \gg C_a$,
2. steady and continuous VOC discharge, wastewater flow and gas ventilation rates,
3. steady-state solution of VOC concentration ($t \rightarrow \infty$).

Equations (14) and (15) can then be solved simultaneously to yield

$$C_l = C_{lo} \exp\left\{\frac{-K_L a}{U_l}\left[1 - \frac{1}{G+1}\right]x\right\} \qquad (16)$$

$$G = \frac{Q_v H_c}{V_l K_L a}. \qquad (17)$$

where,

C_{lo} = VOC concentration in wastewater at $x=0$, M/L^3.

The term G is a dimensionless variable which represents the effects of finite ventilation on mass transfer reduction associated with VOC accumulation in a sewer headspace.

The reach length that corresponds to 50 percent stripping efficiency (half-length $= x_{1/2}$) can then be solved by setting $C_l/C_{lo} = 0.5$ and taking the natural logarithm of each side of equation (16) such that:

$$x_{1/2} = \frac{0.693\, U_l V_l}{K_L A\left[1 - \frac{1}{G+1}\right]}. \qquad (18)$$

Values of K_L and other parameters determined for each of the four Guelph experiments were substituted into equation (18). To assess the effects of ventilation magnitude on half-length, headspace ventilation rate was allowed to vary from 0.3 to 100 turnovers per day. Results are plotted in Figure 4.

Half-length was determined to be highly sensitive to ventilation rate for ventilation rates of less than five turnovers per day. At a ventilation rate of 0.3 turnovers per day, half-lengths ranged from 74 km for Experiment 1.1 to 34 km for Experiment 2.1. At a ventilation rate of 100 turnovers per day, half-lengths varied from 13 km for Experiment 1.1 and Experiment 1.2, to 1.0 km for Experiment 2.1. For all intents and purposes, values of half-length for experiments in Guelph #1 were constant for ventilation rates of greater than 10 turnovers per day. This suggests that an assumption of infinite ventilation is valid for Guelph #1 if the headspace ventilation rate exceeds 10 turnovers per day. Results also indicate that at ventilation rates of less than five turnovers per day, long reach lengths would be necessary to strip 50 percent of 1,1,1-trichloroethane.

Half-length for Guelph #2 continued to decrease for ventilation rates greater than 100 turnovers per day. Thus, an assumption of infinite ventilation in Guelph #2 could lead to significant overestimation of VOC emissions. Nevertheless, even at ventilation rates as low as five turnovers per day, short reaches of sewer can lead to relatively high VOC stripping efficiencies given appropriate sewer operating conditions, e.g., steep channel slope and low depth of flow.

The effects of ventilation magnitude and pattern on VOC emissions from sewers have been described elsewhere [*34*, *35*]. It has been reported that VOC stripping efficiency is far more sensitive to ventilation magnitude than to ventilation pattern. For example, assumptions of uniform ventilation, i.e., equal ventilation inflows and outflows distributed along the length of a sewer reach, and flow-through (co-current) ventilation patterns generally lead to near identical VOC stripping efficiencies. For this study, the CORAL model [*7*] was used in addition to equations (16) and (18) to estimate VOC stripping efficiencies and half-lengths for co-current ventilation. In all cases, half-lengths predicted by CORAL and equation (18) differed by less than 3 percent.

Finally, VOC stripping from sewers can be enhanced in regions of near-instantaneous dissipation of potential energy, e.g., drop manholes and pump station wet wells. Mechanisms that cause gas-liquid mass-transfer at sewer drop structures have also been described elsewhere [*36*]. The effects of sewer drop structures were not considered in this study.

CONCLUSIONS

For the four field experiments described in this paper, values of K_L varied by an order of magnitude, from a low of 0.014 m/hr to a higher of 0.15 m/hr. The latter is believed to approach an upper-bound for most sewer systems. Uncertainties in experimental K_L were estimated to be less than a factor of two.

The experimental data associated with this study were combined with those obtained from previously reported studies. The resulting set of data was compared with the rate of potential energy dissipation (*US*) for each experiment. Over all experiments, a strong correlation was observed between K_L and *US*, with proportionality and power constants nearly equivalent to a diffusivity-adjusted oxygen transfer model published previously. Differences in values of K_L determined in the field and predicted using the aforementioned model were generally less than experimental uncertainty on an experiment-by-experiment basis.

Finally, physical conditions and K_L values determined for the experiments described in this paper were used to predict sewer half-lengths necessary to strip 50 percent of 1,1,1-trichloroethane. Half-lengths ranged from a low of 1.0 km for the maximum K_L and ventilation rate, to a high of greater than 70 km for the minimum K_L and ventilation rate. These results indicate the importance of appropriate determination of both K_L and ventilation magnitude for estimating VOC stripping from sewer reaches.

The information provided in this paper is intended to serve as a basis for future studies of VOC emissions from municipal and on-site industrial sewers. The experimental protocols should serve to facilitate future studies.

ACKNOWLEDGMENTS

This overall research effort has been funded by the Ontario Ministry of the Environment and has been guided by a knowledgeable steering committee, chaired by Mr. Ron Seca. The field experiments were carried out with a great deal of cooperation from the City of Guelph's Department of Waterworks. Chris Quigley of the University of Guelph contributed significantly to field experiments and technical review of this manuscript. Sandra Ausma, Graham Gagnon, Perry Martos, Jennifer Shepherd and Doug Thompson also contributed to field experiments and laboratory analyses. We wish to thank Ms. Diane Duncan for her assistance with graphics. Finally, the authors would like to dedicate this paper to our original research contract manager, the late Rob Paine.

This research was completed while Dr. Richard L. Corsi was a faculty member in the School of Engineering at the University of Guelph. All correspondence concerning this paper should be addressed to Richard Corsi at the University of Texas.

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Effects of High Speed Jets and Internal Baffles on the Gas Residence Times in Large Municipal Incinerators

V. Nasserzadeh and J. Swithenbank
Department of Mechanical and Process Engineering,
Sheffield University, Sheffield, UK

C. Schofield, D. W. Scott and A. Loader
Warren Spring Laboratory, Department of Trade and Industry, Stevenage, UK

The value of knowing the gas residence times in large municipal incinerators and the serious error imposed by the traditional use of gas volume flow rate based average residence time with regard to these incinerators are recognized. There is increasing public awareness and concern over emissions from municipal solid waste incinerators. Modelling studies of particle trajectories using computational fluid dynamics shows the utility of simulation for the determination of residence time distribution in incinerators. These studies indicate that residence time distributions contain valuable information, important to the understanding and evaluation of mixing processes in the incinerator overfire region. A number of design modifications and changes in operational conditions (which have a major influence on the mean gas residence times and overall performance of two large municipal incinerator plants (35 MW and 65 MW) are proposed. Specifically, the effect of high speed jets and different internal baffle configurations have been investigated using mathematical modelling, in an attempt to obtain optimum combustion conditions. This would increase the mean gas residence times, minimize the emission of pollutants and improve the temperature profile throughout the system. The utility of having detailed RTD information for the incinerator overfire region is demonstrated by estimating the residence times using numerical simulation of tracer injection into the 3-dimensional reacting flow field of two typical municipal incinerator configurations. The modelling results not only underscore the critical role played by jets in achieving desirable states of mixing in the overfire region but also point to the significance of the geometry effects.

This modelling work has yielded important results, all of which clearly could not be experimentally verified at the industrial scale due to practical and cost limitations. Nevertheless, the results guide specific modifications to the design and operation and this new approach will be of considerable use to the incinerator design community.

INTRODUCTION

At present around 8 percent of the total UK waste of 29 million tons is burned in 34 large mass burn MSW incinerators, with most of the remainder being landfilled [*1*]. Incineration currently has a high profile resulting from public concern over emissions of pollutants such as particulates, heavy metals, acid gases and dioxins. The regulatory position regarding MSW incineration has undergone considerable changes within the past two years, including the introduction of two Directives from the EC and regulation in the UK under the control of Her Majesty's Inspectorate of Pollution. The Directives set a range of emission limits for pollutants emitted to the atmosphere as well as specifying a number of operating conditions designed to improve the operating efficiency with respect to organic compounds. New plants have been subjected to these limits from December 1990, while existing large MSW plants will be required to reach the new plant standards by December 1996.

Most of the MSW incinerator plants in the UK were built

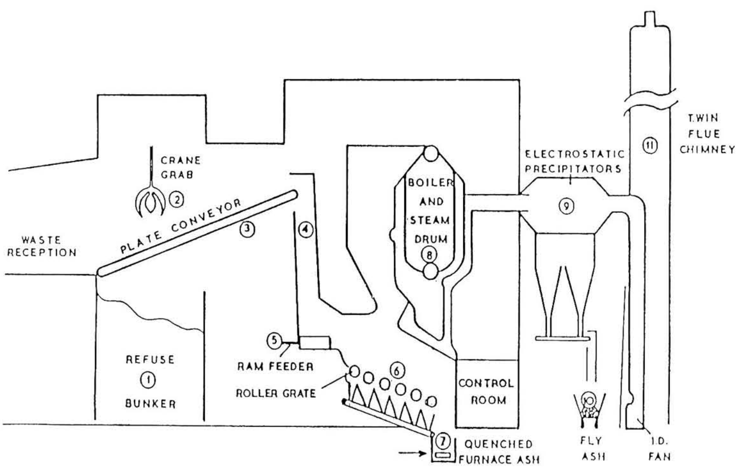

FIGURE 1. Schematic diagram of Sheffield MSW incinerator.

in the late sixties and early seventies with furnace units sized between 5 to 16 metric tons per hour. None of these plants were built with environmental factors, such as pollution emission control, as a high priority. Most plants are fitted with electrostatic precipitators to control particulate emissions but no acid gas control is fitted in any UK incinerator plant [*1*]. It is unlikely that many of them could meet the requirements of the EC Directives. The main priority for these plants at the time of building was the disposal of refuse at the lowest possible cost. Very few of the plants are identical and because of various shortcomings in combustion control, most plants have been modified by the operators in the light of their experience. Most investigations by the Warren Spring Laboratory in recent years, indicated that the performance of some of the existing UK incinerators was poor with respect to pollutant emissions [*1*].

However, in several cases, changes in operational strategies have produced marked improvements. Preliminary calculations show that some of the best UK plants have theoretical residence times of about 2.5 seconds, but actual residence times are probably much lower, due to the suspended dead spaces and recirculation within the combustion chambers. However, it may be possible to minimize all these effects (i.e., raise actual residence times, improve the temperature profiles and reduce concentrations of products of incomplete combustion) by adopting new operational strategies aimed at optimizing combustion and modifying the incinerator design.

Until recently, a relatively small proportion of the effort expended on municipal incinerators has been devoted to investigating the effects of their design and operational performance on the gas residence times and the formation and emission of the pollutant species of concern, i.e., Dioxins. The research work on which this paper is based was oriented toward bridging this gap in the state of art by providing the information which would identify the steps required to achieve acceptably long residence times and low emission levels, and provide a basis for the future design and development of municipal incinerators capable of meeting the required emission goals.

In recent papers ([*3*], [*4*], [*5*] and [*6*]), the authors have outlined the detailed results obtained from the experimental and modelling work carried out on the Sheffield and Coventry MSW incinerators. This paper presents the findings of the modelling studies carried out at Sheffield University, which applied the finite difference techniques to determine the gas residence time distributions for the Sheffield and Coventry MSW incinerators. The main objectives of this study were: 1) to calculate the mean gas residence times for the existing incinerator designs, and 2) to investigate the effect of the design variables and operational parameters on these residence times.

DESCRIPTION OF SHEFFIELD MUNICIPAL INCINERATOR

The incinerator plant which is located centrally in the City of Sheffield came into operation in 1975. It is a two stream × 10 tons/hour plant fitted with steam raising boilers of conventional water tube design. Gas cleaning is by twin electrostatic precipitators. The plant incorporates steam to high pressure hot water heat exchangers to enable heat export to about 10,000 houses and commercial premises in the area. The maximum evaporation rate of each boiler is 31.8 tons of steam/hr with an estimated boiler efficiency of 57.8 percent. When burning refuse with an average gross calorific value of 11,000 kJ/kg, each furnace will produce 24.4 mW or 57×10^6 kJ/hr of continuous maximum output of useful heat for export. The general schematic diagram of the plant is shown in Figure 1. Table 1 presents the brief details of the equipment.

DESCRIPTION OF COVENTRY MUNICIPAL INCINERATORS

The Coventry municipal incinerator plant (65 MW, with a burning capacity of approximately 900 tons/day) became fully operational in 1974. The plant consists of three incinerator units, each with two adjacent grates with five reciprocating sections. Each furnace is capable of handling 12 tons/hour of wet refuse and is fitted with a heat recovery boiler. Incinerator units two and three have water tube boilers, while incinerator unit one has a water tube/fire tube system. The maximum evaporation rate of each boiler is 33 tons of steam/hr with an estimated boiler efficiency of 58.5 percent. The steam produced is sold as process stream to a nearby Talbot engine works. Because of the differences in the design of the heat exchange units, it is likely that emissions from the incinerators will be

Table 1 Sheffield Incinerator Details

Number of units installed	2 units
Furnace grate type	Dusseldorf type
Number of boilers installed	2 boilers
Type of boiler package	2 water tubes
Designed burning rate/unit	10.0 tons/hour
Grate residue ash rate/each unit	2.2 tons/hour (wet)
Electrostatic precipitator flyash rate/hour	0.204 tons/hour (dry)

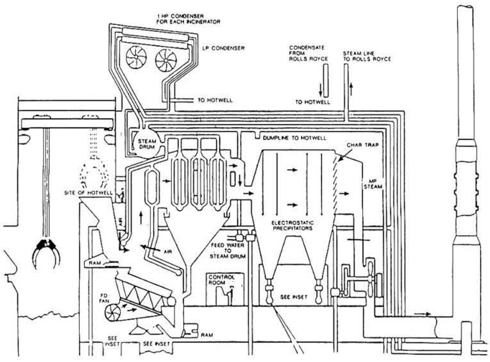

FIGURE 2. Schematic diagram of Coventry MSW incinerator.

significantly different. The plant is normally run with two units operating continuously and one in reserve. A schematic arrangement of the Coventry waste reduction plant is shown in Figure 2. The flue gases from the incinerator/boiler units are drawn through two parallel electrostatic precipitator units by induced draught fans. Alternatively, the combined flue gases from both operational furnaces can be drawn through only one of the precipitators. After leaving the precipitators the gas flows combine and are passed through a short rectangular duct to the 92 m high stack. When in operation, an auxiliary oil fired system discharges into the same stack. Table 2 gives the details of the equipment.

EQUATIONS OF MOTION OF A PARTICLE

A mathematical model of the finite difference type (FLUENT) was used to predict the three dimensional reacting flows (gaseous phase) within both incinerator geometries. A two step kinetic scheme, together with Magnussen type model [7] was used to show chemical reactions. The set of governing equations is given in Appendix 1. Experimental measurements of gas composition, temperature, and exit velocity were compared with model predictions for both incinerators. Modelling results correctly indicated trends and were invaluable for the interpretation of the incinerator performance data. Details of the experimental and modelling work for both incinerators, Sheffield and Coventry, are given in [*3*] and [*5*] respectively.

A Lagrangian type model was used for the calculation of the residence time distributions. In this model, in order to introduce tracer particles into the general procedure, it is convenient to solve the equations of motion and trajectory of a very small particle. The particle is tracked in a Lagrangian frame of reference, with its path through each finite difference cell broken into a number of time steps. When all external effects except drag and gravity are neglected, the equations of motion in Cartesian coordinates can be written as [*8*]:

$$\frac{dx}{dt} = u_p$$

$$\frac{dy}{dt} = v_p$$

$$\frac{dz}{dt} = w_p$$

Here, the subscript p refers to the particle. The gas velocities vary throughout the flow field, and the values used are those prevailing in the finite difference cell which the particle occupies at any given moment. The above formulation contains the assumption that the second phase is sufficiently dilute, so that particle-particle interactions are negligible. The equations of trajectory are solved by step-wise integration at each time step. This method has been found to be advantageous in terms of execution speed with minimal loss of accuracy, and is valid provided the time step is sufficiently small. Solving the equations of motion permits the trajectories of individual particles to be followed. By carrying this out for an ensemble of particles for different initial conditions, it is possible to construct an entire particle laden stream.

A stochastic particle tracking method has also been developed which allows the inclusion of the instantaneous values of the fluctuating components in the gas flow velocities appearing in the equations of motion:

$$U = u_{\text{mean}} + u'$$

The values of u', v', and w', which prevail during the lifetime of a fluid eddy that the particle is traversing, are sampled by assuming that they, obey a Gaussian probability distribution, so that:

$$u' = \zeta \langle (u'^2)^{1/2} \rangle$$

where ζ is a normally distributed random number and the remainder of the right hand side is the local r.m.s. value of the velocity fluctuations. Since the kinetic energy of turbulence is known for turbulent flow calculations, these values of the r.m.s. fluctuating components can be obtained (assuming isotropy) as:

$$\langle (u'^2)^{1/2} \rangle = \langle (v'^2)^{1/2} \rangle = \langle (w'^2)^{1/2} \rangle = \left(\frac{2k}{3}\right)^{1/2}$$

The value of the random number chosen is applied for the characteristic lifetime of the eddy, defined as:

$$\tau = \frac{C_\mu^{3/4}}{2^{1/2}} \frac{k}{\epsilon}$$

after which a new value of ζ is chosen. The values of u, v, w $\langle (u'^2)^{1/2} \rangle$, $\langle (v'^2)^{1/2} \rangle$ and $\langle (w'^2)^{1/2} \rangle$ are updated whenever migration into a neighboring cell occurs. When these two time constraints are combined, a time interval is obtained during which the gas flow velocity remains constant. This permits the direct integration of the equations of motion to obtain a local closed form solution. When particle migrated into a boundary cell, it was assumed that the particle "ricoched" off the boundary in question as if it had a coefficient of restitution of unity (or other set value).

Table 2 Conventry MSW Incinerator Details

Number of units installed	3 units
Furnace grate type	Martin Reverse Acting Reciprocating Grate
Number of boilers installed	Three boilers
Type of boiler package	Two water tube boilers and one water tube/fire boiler
Design burning rate/unit	12 tons/hr
Grate residue ash rate/unit	1.87 tons/hr
Electrostatic precipitator flyash rate/unit	0.38 tons/hr

NUMERICAL SOLUTION

Sheffield Municipal Waste Incinerator Model

To model the Sheffield MSW incinerator (35 MW), Cartesian coordinates with $30 \times 38 \times 9$ grid nodes were used in the vertical (x), length (y) and width (z) directions, respectively, to model the incinerator. FLUENT code (version 2.95) was used for the modeling work. The undergrate air distributions along the grate were set as 86 percent primary air and 14 percent secondary combustion air. A detailed description of the flow field was calculated and key information such as velocity vector plots, temperature profiles and emissions levels were obtained [*3* and *4*].

After the gas phase solution for the incinerator model was obtained, a Lagrangian type model was used to estimate the residence times for the existing incinerator design. Eight trace input positions were investigated computationally. For the computation results, 20 'neutrally buoyant particles' were tracked for each inlet location (in total 140 particles for each case) to obtain an adequate statistical sample. The input position were:

1-through the front and rear secondary air ports,
2-through the undergrate ports (top of rollers 1 to 6).

All tracer output measurements were made at the combustor exit.

The particles were injected close to the undergrate air inlet on top of each grate section, with velocity components of zero in the x and z directions and a vertical velocity equal to the velocity of the primary air inlet flows. The initial temperature was set to 300 K and the particle diameter specified as 5 μm. The total mass flow rate of particles with this set of initial conditions was set to 10^{-7} kg/sec. The density of inert material was set to 1000 kg/m^3.

Coventry Municipal Solid Waste Incinerator Model

The FLUENT code (version 2.95) was used to construct the three dimensional model of the Coventry incinerator. The full geometry of the incinerator was modeled using $32 \times 60 \times 15$ nodes in x, y, and z directions, respectively. The combustion air proportions used for the modeling work were 65 percent primary air and 35 percent secondary air. The undergrate air distributions along the grate were set as 19 percent, 30 percent, 27 percent, 17 percent and 7 percent for grate sections 1 to 5, respectively. A detailed description of the flow field was calculated and key information such as velocity vector plots, temperature profiles, emissions levels and estimates of the degree of mixing between fuel rich and air rich portions of the flow were obtained [*5*].

Again a Lagrangian model was used to estimate the gas residence times for the Coventry municipal incinerator. Seven trace input positions for each case were investigated computationally. For the computation results, 20 'neutrally buoyant particles' were tracked for each inlet location (in total 140 particles for each case) to obtain an adequate statistical sample. The input positions were:

1-through the front and rear secondary air ports,
2-through the undergrate ports (top of grate sections 1 to 5).

All tracer output measurements were made at the combustor exit. The particles were injected close to the undergrate air inlet on top of each grate section, with velocity components of zero in the x and z directions and a vertical velocity equal to the velocity of the primary air inlet flows. The initial temperature was set to 300 K and the particle diameter specified as 5 μm. The total mass flow rate of particles with this set of initial conditions was set to 10^{-7} kg/sec. The density of inert material was set to 1000 kg/m^3.

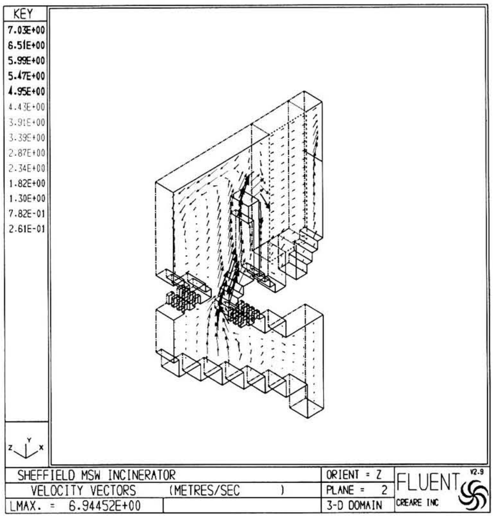

FIGURE 3. Predicted velocity vector plot for Sheffield incinerator.

RESULTS

Figures 3 and 4 show the velocity vector plot and the particle trajectories for different particle injection locations (top of rollers 1 to 6 and the secondary air inlets) for the Sheffield incinerator plant, respectively. The modeling results showed that a considerable fraction of the total gas flow was trapped in large eddies (dead volumes) located at the discharge end of the travelling grate and the left hand corner of the radiation shaft. This flow spent much more than the average length of time (>2 seconds) in the furnace, while the rest of the flow took place through a restricted channel near to the rear arch of the furnace. Particles trapped in these eddies had a relatively long residence time.

As can be expected from the structure of the flow field (Figure 3), particles injected from the top of rollers 2, 3 and

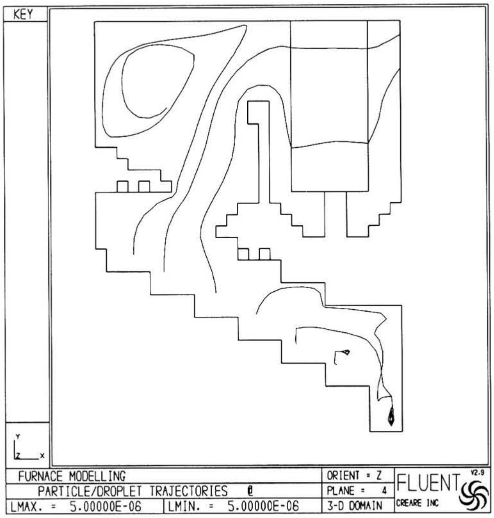

FIGURE 4. Predicted particle trajectories for Sheffield incinerator.

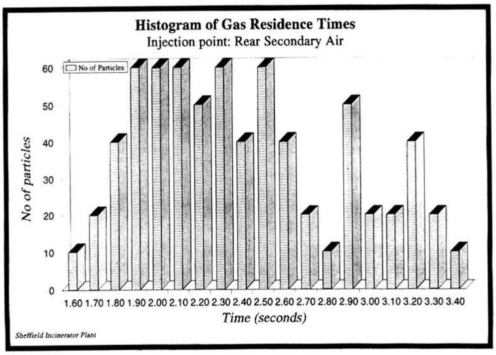

FIGURE 5. Typical histogram of gas residence times for particles injected from rear secondary air inlet.

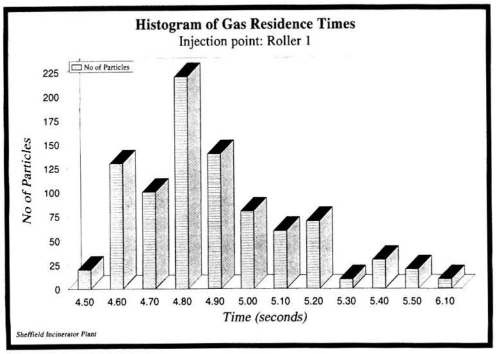

FIGURE 6. Typical histogram of gas residence times for particles injected from the top of roller number one.

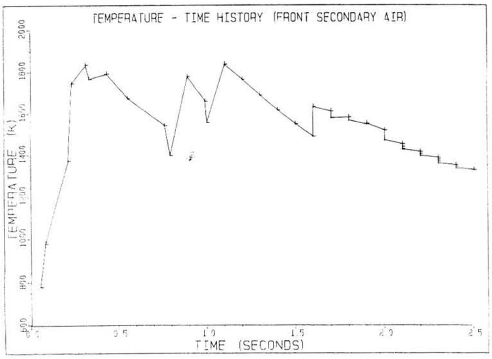

FIGURE 8. Temperature vs. time plot along the path of particles injected from the secondary air inlet.

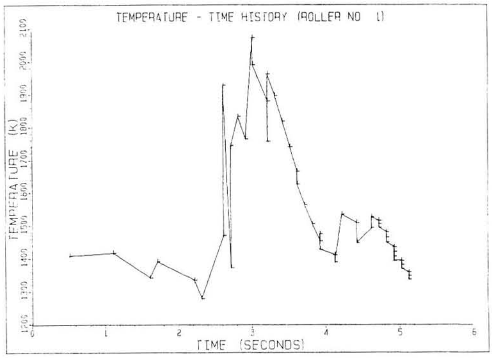

FIGURE 9. Temperature vs. time plot along the path of particles injected from the top of roller one.

4 and 78 percent of the total number of particles injected from the secondary air inlets followed the gas flow of the relatively high velocity and escaped from the combustor without entering the recirculation zone in the shaft. Thirty-eight percent of the injected particles from the front secondary air inlets and top of roller one were captured by the corner part of the recirculation zone in the shaft, therefore having significantly long residence times. Typical histograms of gas residence times for different tracer input positions are given in Figures 5, 6 and 7.

Possible errors in the results obtained from the FLUENT modeling work are likely to be due to:

1) the use of computed flow field instead of a measured one,
2) the use of the $k-\epsilon$ model results to approximate the Lagrangian information, and
3) the possible existence of some computational dead time on the small difference cell.

Nevertheless, the modeling results obtained here, are generally satisfactory and confirm the validity of this method of extracting residence time distribution information from the finite difference modeling.

The typical time evolution of temperature variations along the path of each injected particle throughout the system was

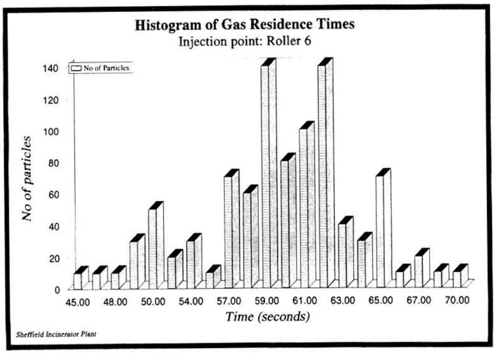

FIGURE 7. Typical histogram for gas residence times for particles injected from the top of roller number six.

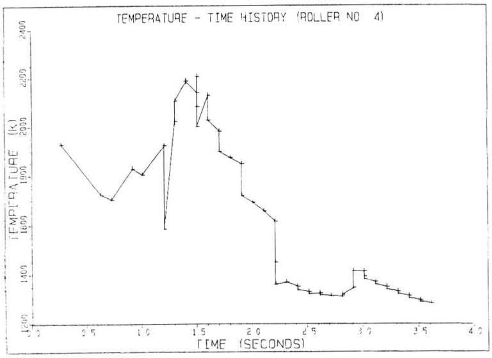

FIGURE 10. Temperature vs. time plot along the path of particles injected from the top of roller four.

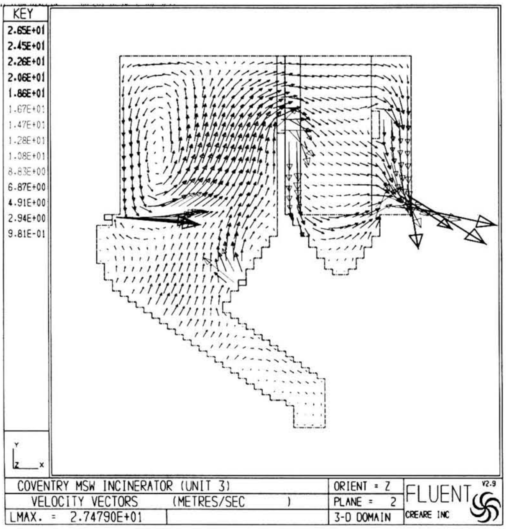

FIGURE 11. Predicted velocity vector plot for Coventry incinerator.

also recorded. Figures 8, 9, and 10 show the typical predicted temperature—time history plots for particles injected from different points. The predicted temperature variations versus time plot for the particles injected from the secondary air inlets (both front and rear) showed that nearly 71 percent of these particles were held at temperatures >1200 K for about 2 seconds before leaving the shaft. The remaining particles injected from the front secondary air were captured in the recirculation zone (temperatures <900 K) and were held there for quite a long time. These particles did not enter the hot firing zone at all. The majority of particles injected from the top of rollers 1, 2, and 3 (apart from those trapped in the recirculation zone in the shaft) spent most of their journey time at high temperature firing zone located near to the rear arch of the furnace. The temperature time history plots for the particles injected from top of rollers 4, 5, and 6 showed that most of these particles were held at low temperatures (trapped in the recirculation zone at the discharge end of travelling grate) for sometime before finally entering the firing zone and leaving the shaft.

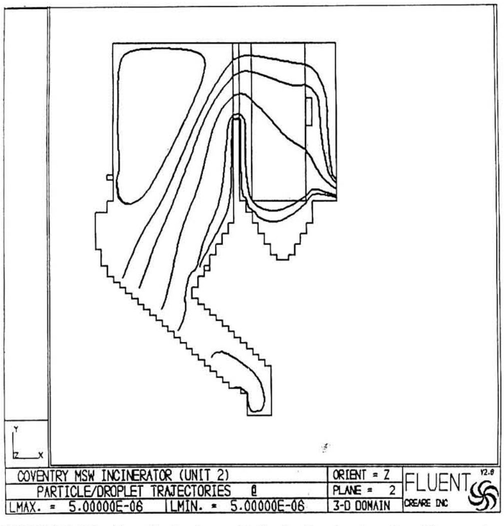

FIGURE 12. Predicted particle trajectories for Coventry incinerator.

Figures 11 and 12 show the velocity vector plot and particle trajectories for different particle injection locations (top of grate sections 1 to 5 and secondary air inlets) in the plane of the secondary air jets for the Coventry MSW incinerator. Because the gas flow is turbulent, a random nature of the particle tracks exists despite identical initial conditions.

The modeling results show that a considerable fraction of the gas flow took place through a restricted channel near to the rear arch of the furnace. As can be expected from the structure of the flow field, particles injected from the top of grate sections 2, 3, and 4 and nearly 98 percent of the total number of particles injected from the secondary air inlets followed the gas flow of relatively high velocity and escaped from the combustor without entering the recirculation zone in the shaft. Thirty-seven percent of the injected particles from the front secondary air inlet and top of grate section one were captured by the corner part of the recirculation zone in the shaft, therefore having a significantly long residence times.

Particles injected from the top of grate sections 4 and 5, with initial velocity equal to the undergrate air velocity, collided with the furnace roof and moved slowly downward toward the grate where recirculation tended to occur. Most of these particles were halted by the maximum number of time integration steps (32,000 steps). In particular, those particles injected from the top of grate section 5, tended to recirculate internally and form a relatively dense layer of particles on top of the grate.

Overall, the majority of particles injected from different positions on top of grate had a mean residence time greater than 2 seconds. The predicted mean gas residence times for the particles injected from both the front and rear secondary air inlets varied between 0.7 to 1.6 seconds. The above results clearly illustrate that the residence time of the injected particles depends strongly on their initial injection points.

Typical histograms of the residence time of the injected particles are shown in Figures 13, 14 and 15. The main purpose of drawing the histograms was to display a representation of the shape of the distribution of the data values. The rear secondary air histogram showed the crowding on the left whilst the columns became shorter toward the right, indicating that most of the particles injected from this point had a short residence time between 0.7 and 1.2 seconds. The histogram for the particles injected from the front secondary air looked quite similar to the one for the rear secondary air jets. Most of the data concentrated very near to the left, with a long tail extending to the right. The histogram for grate section one skewed slowly toward the right. The majority of particles in this case had a residence time between 2.0 to 3.10 seconds. The majority of the particles injected from the top of grate 5 had a residence time of 11.1 seconds and were represented in

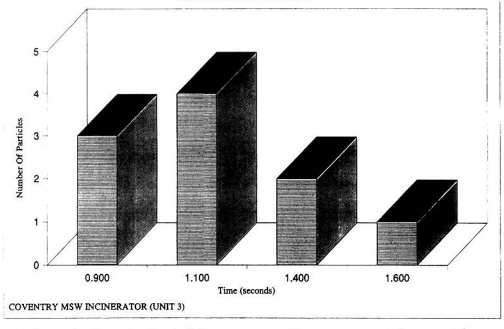

FIGURE 13. Typical histogram for gas residence times for particles injected from front secondary air inlet.

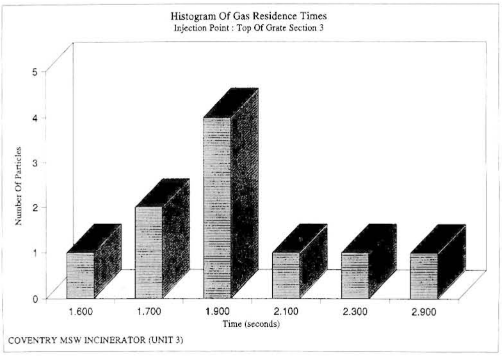

FIGURE 14. Typical histogram of gas residence times for particles injected from top of grate section three.

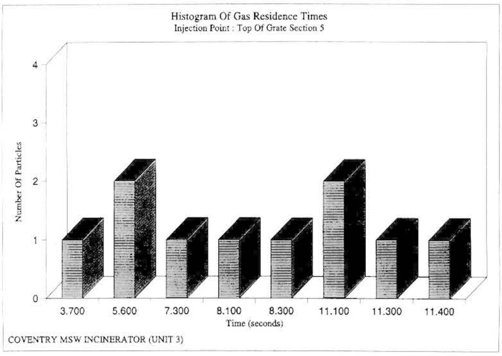

FIGURE 15. Typical histogram of gas residence times for particles injected from top of grate section five.

the single column on the far right. The histogram for the particles injected from the top of grate section 5 showed random variations in the occurrence of the residence times that were close to one another.

Temperature-time history plots for different particles injected from different positions for the existing incinerator design (unit 3) are given in Figures 16 to 18, respectively. As shown, the majority of the total number of particles injected from the top of the grate flowed through the hottest part of the firing zone (temperatures >1200 K) at the base of the radiation shaft with an average residence time of 2 seconds.

The predicted temperature variations versus time plot for the particles injected from the secondary air inlets (both front and rear) showed that nearly 68 percent of these particles were held at temperature >1200 K for about 1 second before leaving the radiation shaft. The remaining particles injected from the front secondary air were captured in the recirculation zone (temperatures <1200 K) and were held there for relatively long periods. These particles did not enter the hot firing zone at all. The majority of particles injected from the top of grate sections 1, 2, and 3 (apart from those trapped in the recirculation zone in the shaft) spent most of their journey time in the high temperature firing zone located near to the rear arch of the furnace. The temperature variation versus time plots for the particles injected from the top of grate sections 4 and 5 showed that most of these particles were held at lower temperatures (trapped in the recirculation zone at the discharge end of the travelling grate) for sometime before finally entering the firing zone and leaving the shaft.

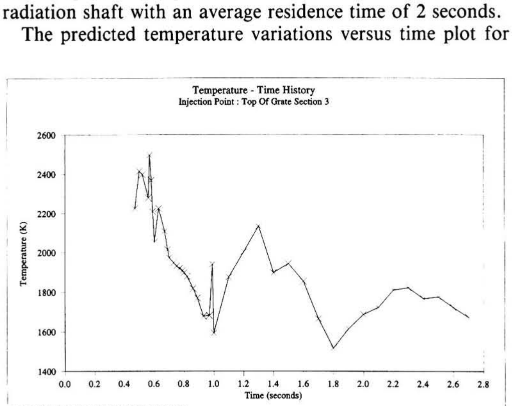

FIGURE 16. Temperature vs. time plot along the path of the particles injected from the top of grate section three.

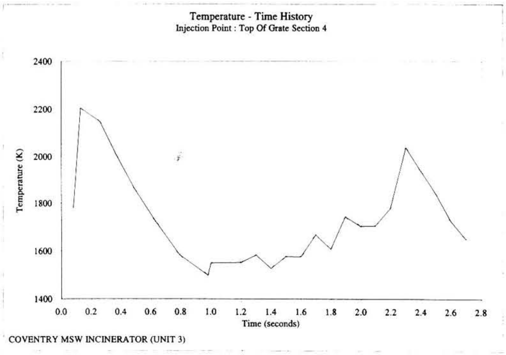

FIGURE 17. Temperature vs. time plot along the path of the particles injected from the top of grate section four.

A SUGGESTED DESIGN MODIFICATION AND Its EFFECT ON THE MEAN GAS RESIDENCE Time

CFD models were used to investigate the critical role played by the large high speed secondary air jets in achieving a desirable state of mixing and longer residence times in the overfire region. Also investigated was the significance of the geometry effect (i.e., installation of baffles inside the shaft) on the mean gas residence times for both the incinerator plants. In our studies, the mathematical models based on the existing plant designs and the experimental data obtained for both plants,

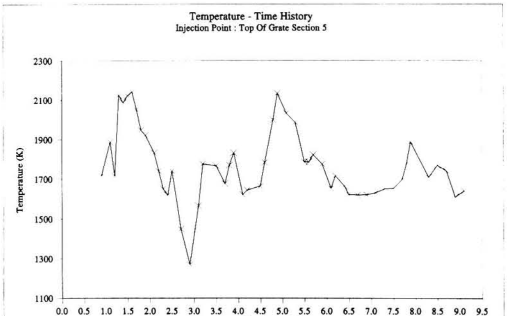

FIGURE 18. Temperature vs. time plot along the path of particles injected from the top of grate section five.

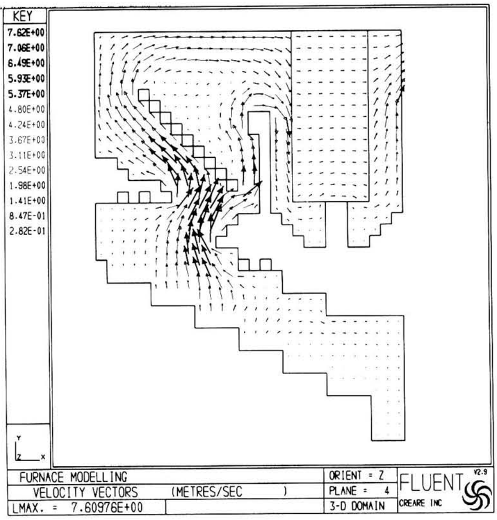

FIGURE 19. Predicted velocity vector plot.

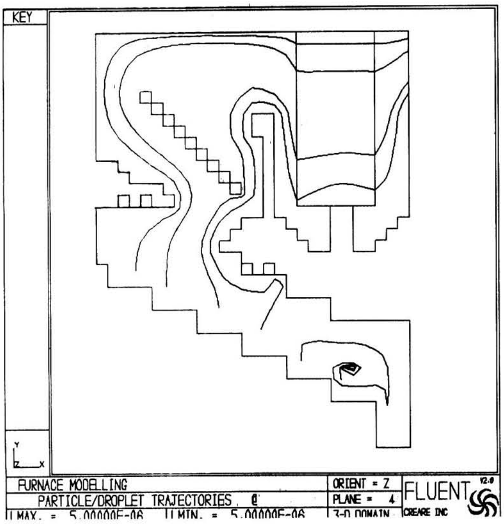

FIGURE 21. Predicted particle trajectories.

confirmed the existence of a large recirculation zone inside the vertical shaft. Details of the proposed design modifications for both plants based on the concept of eliminating the recirculation zone in the shaft, thus increasing mean gas residence times and improving temperature profiles through the system, are discussed in [*3*], [*4*], [*5*] and [*6*].

Sheffield MSW Incinerator

One of the proposed design modifications for the Sheffield MSW incinerator consisted of the introduction of a flat heating surface (Baffle) into the radiation shaft at approximately 60° to the horizontal and located 0.6 m above the nose of the furnace arch. Figures 19 to 21 show the predicted velocity vector plot, predicted temperature profile and the particle trajectories for different particle injection locations for this case. As shown, the presence of a baffle has resulted in lower gas velocities in the shaft which thereby retains the burning gases in the zone of active combustion (temperatures >1200°C) for a longer period of time. The predicted gas residence times for this modified design were about twice those calculated for the existing design.

The effect of high speed secondary air jets on both the overall performance of the Sheffield incinerator and the gas residence times was also investigated using CFD models. Here, in the proposed design, instead of having a very large number of secondary air injection ports (44 jets in total) in the same horizontal plane, eight large secondary injection ports are situated on a plane at an angle of 45° to the vertical (Figure 22). Each jet is positioned on the side wall at 75 cm separation and is fired into the main flow tangentially to a rotational circle (at a 30° angle to the horizontal). The main feature of this design is the formation of a very strong recirculation zone due to the high speed secondary air injections. Unlike the existing incinerator design in which a recirculation zone occurs in the shaft, when the eight high speed injections are introduced, the flow field is changed dramatically. The recirculation zone inside the shaft which was present in the existing incinerator

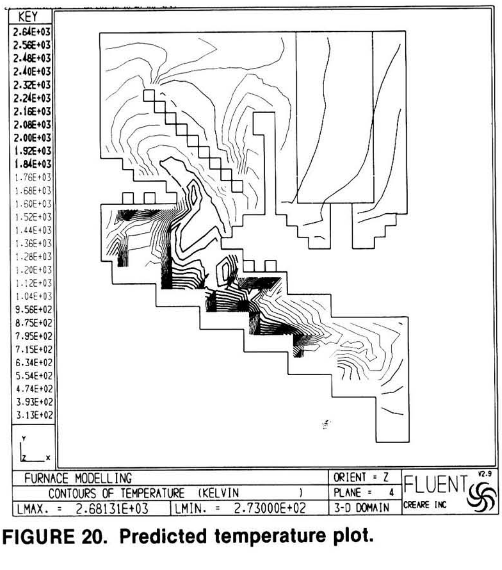

FIGURE 20. Predicted temperature plot.

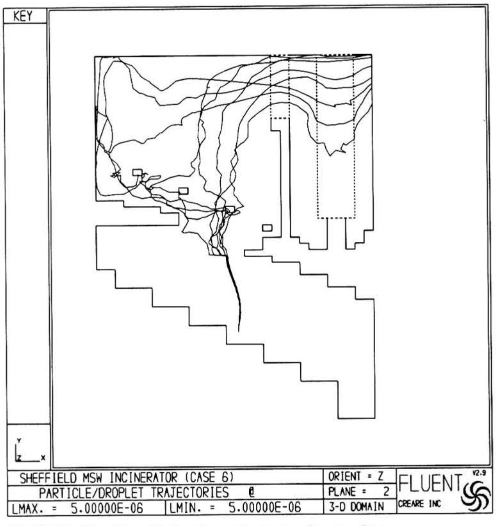

FIGURE 22. Predicted particle trajectories.

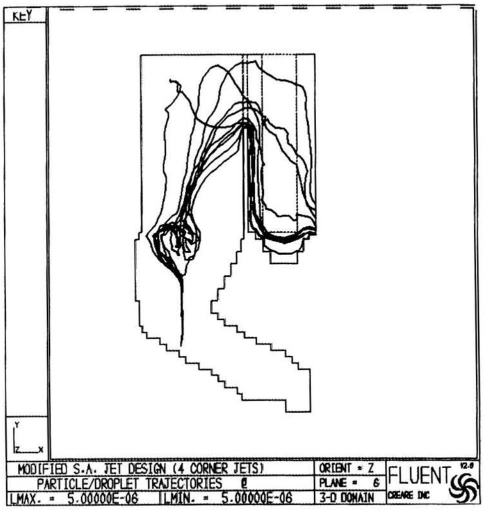

FIGURE 23. Predicted particle trajectories plot.

design, has disappeared and the main flow out of the furnace is directed towards the middle of the shaft. As expected from the structure of the flow field in this design, the entire volume of the radiation shaft is used as true combustion space with no dead spaces. Hence marked improvements in heat exchange are achieved with this system compared to the original incinerator design. Due to the presence of the large recirculation zone above the burning refuse bed near to the middle of furnace shaft, the burning gases evolving from the top of the bed are retained in the zone of active combustion at temperatures well above 1200°C for a substantially long period of time before entering the convection heat transfer section of the unit. The results show marked improvements in mixing characteristics and mean gas residence times in this design compared to the values obtained for the existing incinerator design.

Coventry MSW Incinerator

The suggested design modifications for the Coventry MSW incinerator consisted of four high speed air jets (76 m/sec) positioned at each corner of the furnace shaft above the nose of the furnace arch and firing towards a common center at 90° to the vertical. Figure 23 shows the particle trajectories for this case. As shown, the main feature of this design is again the formation of a strong recirculation zone due to the four high speed secondary air injections. Recirculation zones are usually formed in flows when the effect of an adverse axial pressure gradient exceeds the kinetic energy of fluid particles and a stagnation point is produced. Unlike the existing incinerator design, in which a dead one occurs in the shaft, when the four high speed injections are introduced, the flow field is changed dramatically. The central part of the recirculation zone appears in the middle of the furnace shaft. It is a strong recirculation zone which plays a crucial role in the stabilization and intensification of combustion. In the modified design the dead zone inside the shaft, which was present in the existing incinerator design, has disappeared and the main flow out of the furnace is directed towards the middle of the shaft. Again, the entire volume of the radiation shaft is used as true combustion space with no dead spaces and hence marked improvements in heat exchange are achieved with this system compared to the original incinerator design.

In addition to the increase in gas residence times, modeling results suggest that the new modified design could produce very low flyash carry-over (particulates emissions) from the incinerator. In the proposed design, the secondary air introduced directly at the base of chimney acts somewhat as a "blanket" and prevents, to some extent, the entrainment of the flyash by the products of combustion due to the presence of the stagnation zone at the base of shaft. Also, the presence of the recirculation zone results in a 'down flow' of the flyash laden flue gas. The inertia of the particles, combined with gravity and the secondary air jet configuration, is expected to assist in the separation of the heavy flyash particles from the gas stream, preventing a considerable portion of the flyash from being entrained into the radiation shaft and the boiler section. The results show a marked improvement in mixing characteristics and mean gas residence times in this design compared to the values obtained for the existing incinerator design.

CONCLUSIONS

Modeling studies of particle trajectories using computational fluid dynamics shows the utility of simulation for the determination of residence time distribution in incinerators. These studies indicate that RTD's contain valuable information that is important to the understanding and evaluation of mixing processes in the incinerator overfire region. The results obtained from our modeling studies for the Sheffield and Coventry municipal incinerators indicate that while the jets are critical to achieving desirable states of mixing in the overfire region, the geometry effects are also significant. Our modeling work clearly indicates that the specific emission and operational goals for the existing municipal incinerators can be achieved with simple modifications of conventional incinerator designs together with the optimization of the plant's overall performance as a function of operating parameters. This modeling work has yielded interesting results, all of which clearly could not be experimentally verified at the industrial scale due to practical and cost limitations. Nevertheless, the results guide specific modifications to the design and operation and this new approach will be of considerable use to the incinerator design community.

ACKNOWLEDGMENTS

This research program was funded by Warren Spring Laboratory (Department of Environment) whose financial support is, hereby, gratefully acknowledged. The authors would also like to thank the staff of the Sheffield Waste Disposal Unit and Coventry MSW Incinerator for their help and co-operation in this project.

NOTATION

A = combustion model constant
C_p = gas specific heat capacity at constant pressure
h = enthalpy
k = kinetic energy of turbulence
M_i = molecular weight of species i
m_i = mass fraction of species i
P = pressure
R = gas constant
R_{CO} = rate of CO consumption by chemical reaction
R_{fu} = rate of fuel consumption by chemical reaction
S_h = enthalpy source term due to chemical reaction
S_s = species source term due to chemical reaction
T = temperature
t = time
u = velocity vector
u_i = time average velocity component

$\tilde{u}_i$ = instantaneous velocity component
u_i' = fluctuating component of u_i
γ_{ij} = Kronecker Delta
ϵ = dissipation rate of k
λ = gas thermal conductivity
ρ = density of gas
τ = turbulence time scale
δ = empirical constant

Subscripts

CO = carbon monoxide
fu = fuel
k = kinetic energy of turbulence
O = oxidant
s = chemical species
ϵ = dissipation rate of k

Abbreviation

MSW = municipal solid waste

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APPENDIX 1—EQUATIONS OF GAS PHASE MODEL

Conservation of Mass:

$$\frac{\partial}{\partial x_i}(\rho u_i) = 0$$

Conservation of Momentum:

$$\frac{\partial}{\partial x_i}(\rho u_i u_j) + (\rho u_i{}') = -\frac{\partial \delta_{ij}}{\partial x_i}$$

$$\delta_{ij} = p\gamma_{ij} - \mu\left[\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right] + \frac{2}{3}\mu\left(\frac{\partial u_i}{\partial x_j}\right)\gamma_{ij}$$

k-ϵ Turbulence Model:

$$\frac{\partial}{\partial x_i}(\rho u_i k) = \frac{\partial}{\partial x_i}\left[\left(\frac{\mu + \mu_t}{\delta_k}\right)\left(\frac{\partial k}{\partial x_i}\right)\right] + P - \rho\epsilon$$

$$\frac{\partial}{\partial x_i}(\rho u_i \epsilon) = \frac{\partial}{\partial x_i}\left[\left(\frac{\mu + \mu_t}{\delta_\epsilon}\right)\left(\frac{\partial \epsilon}{\partial x_i}\right)\right] + C_1\frac{\epsilon}{k}P - C_2\rho\frac{\epsilon^2}{k}$$

$$\mu_t = 0.09 \times \frac{\rho k^2}{\epsilon}$$

Modelling coefficients take the values $C_1 = 1.44$, $C_2 = 1.92$, $\delta_k = 1.0$ and $\delta_\epsilon = 1.3$.

Equation for the Conservation of Enthalpy

$$\frac{\partial}{\partial x_i}(\rho u_i h) = \frac{\partial}{\partial x_i}\left[\left(\frac{\mu + \mu_t}{\delta_h}\right)\left(\frac{alh}{\partial x_i}\right)\right] + S_h$$

Equation for Conservation of Chemical Species

$$\frac{\partial}{\partial x_i}(\rho u_i m_s) = \frac{\partial}{\partial x_i}\left[\left(\frac{\mu + \mu_t}{\delta_s}\right)\left(\frac{alm_s}{\partial x_i}\right)\right] + S_s$$

The Equation of State

$$\rho = \frac{p}{RT\sum m_j/M_j}$$

Abatement of N_2O Emissions Produced in the Adipic Acid Industry

R. A. Reimer
Sabine River Laboratory, E.I. du Pont de Nemours and Co., Orange, TX

C. S. Slaten
Victoria Development Laboratory, E.I. du Pont de Nemours and Co., Victoria, TX

M. Seapan
Corporate Process Development, E.I. du Pont de Nemours and Co., Ponca City, OK

and

M. W. Lower and P. E. Tomlinson
E.I. du Pont de Nemours and Co., Wilmington, DE

Apidic acid (AA) manufacture results in the production of ca. 1 mole of nitrous oxide (N_2O) per mole of AA. Emissions of N_2O by the AA industry currently account for about 5–8 percent of the worldwide anthropogenic N_2O emissions (after accounting for N_2O abated by some manufacturers). Even though this N_2O does not make a major contribution to global warming and ozone depletion, major AA producers worldwide have agreed to substantially reduce these emissions by 1996–98. Producers have formed an inter-industry group to share information on technologies being developed for N_2O control. Technology options being studied by DuPont (and by others) include thermal destruction, recycling, and catalytic decomposition.

INTRODUCTION

Hexanedioic acid, commonly known as adipic acid (AA), is among the top 50 synthetic chemicals produced in the United States each year. Current annual global production is estimated at 1.8 million metric tons [*1*]. The largest use for adipic acid is in the manufacture of nylon 6,6 polyamide via its reaction with 1,6-hexamethylenediamine. Nylon 6,6 polymer, discovered by W. H. Carothers in the early 1930s, is now used in carpets, tire cord, apparel, upholstery, auto parts, and in hundreds of other applications that impact our life in many ways.

Most adipic acid produced in the world today is manufactured from cyclohexane feedstock. Cyclohexane is converted to cyclohexanol (A), or a cyclohexanone (K)/cyclohexanol (A) mixture (KA), and the product KA is purified in the initial synthesis steps. In a second series of process steps, KA is reacted with nitric acid to produce adipic acid, which is then purified by crystallization. As discussed by Castellan et al. [*2*], Nitric acid oxidation of KA results in an unavoidable production of ca. 1 mole of N_2O per mole of AA produced. NO_x is also produced in the HNO_3 oxidation step, and is generally absorbed from the reaction off-gases and re-converted to nitric acid for process recycle.

Table 1 Global Adipic Acid Industry N_2O Emissions Estimates (1990)

	N_2O Made (kt/yr)	N_2O Abated (%)	N_2O Emitted (kt/yr)
DuPont	161	53	76
Total AA Industry	545	32	371
Total AA Industry (TgN)	0.35	32	0.24

Basis: Estimated 1990 worldwide adipic acid production ca. 1.8 Mt

N_2O, contained in reaction off-gases after NO_x recovery, is emitted to the atmosphere by some producers. DuPont (Victoria, Texas) and Monsanto (Pensacola, Florida) have for many years passed the off-gases through reducing furnaces/burners for further NO_x control, which results in coincidental destruction of N_2O [3]. Using individual plant capacity data summarized in reference 1, we estimate that ca. 32 percent of the nitrous oxide produced via adipic acid manufacture in 1990 was destroyed. Thus, as indicated in Table 1, about 545,000 metric tons of N_2O were produced in 1990 via AA manufacture, while about 371,000 metric tons were ultimately emitted [4].

M. H. Thiemens and W. C. Trogler, in a 1991 article in Science magazine [5], called attention to the magnitude of AA industry N_2O emissions relative to those from other anthropogenic sources. They pointed out the possible impact of this N_2O on stratospheric ozone destruction and global warming.

N_2O EMISSIONS AND GLOBAL IMPACT

In 1988, a global forum, known as the Intergovernmental Panel on Climate Change (IPCC), was established to address changes in the Earth's atmospheric composition as a result of natural and anthropogenic fluxes of greenhouse gases [6]. The IPCC subsequently estimated that 6.9-16.4 million metric tons per year of N_2O are emitted globally by natural and man-made sources. Bacterial action in oceans and soils is believed to provide the dominant natural sources of N_2O, while fertilizer degradation and combustion processes are thought to be among the major anthropogenic sources. The major sink for N_2O is believed to be photolysis in the stratosphere, with some removal also by microbial action in soils.

The atmospheric lifetime of N_2O molecules in the environment is estimated at 150 yrs., and recent data show that N_2O in the atmosphere has increased from a pre-industrial era background level of ca. 285 ppbv to a 1990 concentration of 310 ppbv [6]. This corresponds to a recent increase of 0.2-0.3 percent per year or 4.7-7 million metric tons per year from all anthropogenic sources.

Nitrous oxide is a radiatively and chemically active trace gas which is believed to contribute to the recent increase in the Earth's surface temperature by absorbing reflected infrared radiation (the enhanced greenhouse effect). The IPCC study reports that the global warming potential (GWP, 100 year horizon) of each molecule of N_2O emitted is about 290 times that of a carbon dioxide molecule. During 1980-1990 it is estimated that man-made N_2O from all sources contributed about 6 percent to the overall change in climate forcing (for comparison, man-made CO_2 contributed 55 percent and halogenated gases contributed 24 percent) [6].

The impact of man-made N_2O on ozone depletion is less well defined. It is known that approximately 70 percent of natural ozone destruction is due to stratospheric NO, which in turn arises from the presence of N_2O, so that increases in N_2O will eventually result in increased ozone destruction [7]. Considering this information, one might estimate that man-made N_2O could be responsible for about a 6 percent increase in ozone depletion rate. However, when the combined effects of increased CFCs and N_2O are considered, some authors believe that increased N_2O may actually mitigate the CFC-induced ozone decrease [8].

ADIPIC ACID INDUSTRY INITIATIVES

Since adipic acid related N_2O emissions are recognized as making a measurable contribution to global warming and ozone depletion, major adipic acid producers worldwide have agreed to substantially reduce industry emissions by 1996-98.

Major AA producers took an unusual step in July, 1991, by forming an inter-industry group to share information on old and new technologies being developed for N_2O abatement. Four industry N_2O technology exchanges have been held to date, with Asahi (Japan), BASF (Germany), Bayer (Germany), DuPont (USA), ICI (UK), and Rhone-Poulenc (France) participating. (ICI's nylon production facilities were subsequently acquired by DuPont in 1993.) Producers have been able to make better, faster decisions concerning N_2O abatement through this sharing of knowledge. DuPont developed N_2O control technologies will ultimately be made available to other manufacturers.

N_2O ABATEMENT TECHNOLOGY DEVELOPMENT

Abatement technology options currently being studied include: (1) improvements to the commercially demonstrated processes for N_2O decomposition in specially designed boilers, (2) conversion of N_2O to recoverable NO, and (3) catalytic dissociation to N_2 and O_2.

The chemistry of N_2O decomposition has been studied by many researchers over the years. As summarized by Lipkea et al. [9], the primary reaction steps involved in homogeneous thermal decomposition of N_2O are:

$$N_2O + M \rightarrow N_2 + O + M \tag{1}$$

$$N_2O + O \rightarrow N_2 + O_2 \tag{2}$$

$$N_2O + O \rightarrow NO + NO \tag{3}$$

The major reaction products of N_2O decomposition are generally N_2 and O_2. Formation of N_2 and O_2 is exothermic, with a calculated heat of reaction of ca. −20.5 kcal/g mole. Thermodynamics dictate that NO_x formation via reaction (3) will not become significant unless temperatures exceed about 800°C.

The search for economical and efficient methods for abatement of unabsorbed NO_x in adipic acid off-gases began within DuPont shortly after the HNO_3 oxidation process was commercialized in the late 1940s. In 1958, the Orange, Texas plant implemented boiler destruction of NO_x in the off-gases. In addition to NO_x destruction, it was found that conditions in the boilers also facilitated N_2O decomposition. When the Victoria, Texas plant was started up in the late 1960s, this technology was applied there also. Boiler destruction of off-gases was discontinued at Orange in 1987 when a high efficiency NO_x absorber was installed, allowing atmospheric disposition of the gases.

At Victoria the current boiler N_2O destruction technology uses reducing flame burners with premixed methane. The flame temperature is near 1500°C, and both NO_x and N_2O are destroyed as illustrated in the following equations:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \tag{4}$$

Table 2 Typical Adipic Acid Reaction Off-Gas Analysis

Component	Mole %	
N_2O	30.5	(30–50%)
NOx	0.7	
CO_2	6.0	
CO	0.03	
O_2	3.9	
H_2O	2.0	
N_2	57.0	
VOC	0.03	

(DuPont, Victoria: 14,000–28,000 scmh)

$$CH_4 + 4\,N_2O \rightarrow 4\,N_2 + CO_2 + 2\,H_2O \qquad (5)$$

$$CH_4 + 4\,NO \rightarrow 2\,N_2 + CO_2 + 2\,H_2O \qquad (6)$$

As shown in Table 2, Victoria adipic acid off-gases currently fed to the boilers average about 0.7 percent NO_x and 30-50 percent N_2O. The reducing flame burner system has been shown to destroy 98-99.9 percent of the N_2O; but with no significant net reduction in total NO_x. At the high flame temperatures in the burners, sufficient N_2O is decomposed via reaction (3) to result in ca. 1-2 percent conversion to NO_x. This appears to offset any NO_x reduction that may have been achieved in the reducing flame. Stack NO_x levels produced by the current boiler system would ultimately need to be treated by secondary NO_x reduction techniques in order to meet future standards.

Improved burner/boiler systems have been proposed to provide lower stack NO_x levels. A boiler gas reburn system coupled with selective non-catalytic reduction (SNCR) has been designed for the 1994 startup of the new DuPont Singapore plant with the assistance of the Energy and Environmental Research Co. (EER) of Irvine, California. Improved reducing furnace technology has also been developed jointly by Bayer and Drager-Energie-Technik (DET) in Germany. These N_2O and NO_x control technologies are most practical at plant sites where the steam generated from the substantial fuel utilized in these boilers is needed.

In 1990, DuPont began studies of possible processes for conversion of N_2O to recyclable NO. Early studies by Briner *et al.* [*10*], and data summarized in reference [*9*], indicated possible NO yields as high as 0.33 moles per mole of N_2O. Synthesis of NO from N_2O has been considered in the past by DuPont, and more recently by Asahi [*11*]. NO produced by this sort of process could be reacted with oxygen and absorbed using commercial nitric acid technology to produce HNO_3, which would be reused in the manufacture of adipic acid.

In 1991, DuPont contracted with EER to build a pilot scale N_2O to NO reactor. To date, the EER pilot unit has demonstrated N_2O destruction greater then 99.8 percent and yield >0.15 moles NO per mole N_2O. In mid-1992 Rhone-Poulenc joined with DuPont in developing this process. At current yield levels, the recycle process is not economically feasible at DuPont. Work is continuing on yield improvements. A patent is pending.

In 1991, when the possible long-term environmental impact of N_2O emissions became recognized, DuPont began working with several different catalyst manufacturers to develop commercial catalysts for low temperature N_2O decomposition to N_2 and O_2. Catalyst manufacturers involved included: Air Products, BASF AG, Engelhard, ICI Katalco, Johnson Matthey, and UOP.

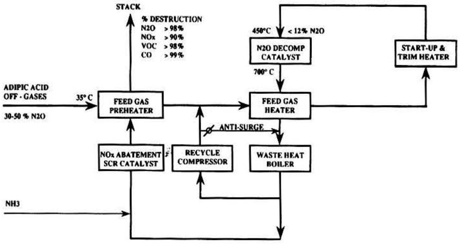

FIGURE 1. Typical process flowsheet for catalytic decomposition of N_2O.

Catalytic decomposition of N_2O has been widely studied and reported in the literature. N_2O decomposition is frequently used as a test reaction in evaluation of oxidation catalysts and characterization of catalytic materials. Early studies of metal oxide catalysts are reviewed by Winter [*12*] and Viswanathan [*13*]. More recent work has focused on developing catalysts with sufficient activity and stability for commercial application in the adipic acid process. Catalysts with commercial potential include Pd/Al_2O_3 [*14*] and metal exchanged zeolites [*15, 16*]. An N_2O decomposition catalyst consisting of NiO and CoO on a zirconia substrate has also been developed within DuPont [*17*].

Economic analyses initiated by DuPont in mid-1992 indicated that catalytic N_2O abatement is the clear economic process choice for implementation at the Orange, Texas site, the Maitland, Ontario site, and the Wilton, UK site in the 1996 time frame. Boiler N_2O abatement at the Victoria site will be phased out in 1998 and replaced with a catalytic system.

DuPont has constructed a 1 cm laboratory isothermal reactor (Ponca City, Oklahoma) and a 5 cm adiabatic pilot unit (Victoria) for use in evaluation of catalyst activity, for life testing of the catalyst candidates, and for process development. Several viable catalyst candidates have been identified and testing is continuing. Issues being studied include: light off temperature, high temperature limitations, catalyst life, N_2O destruction effectiveness, inhibitors, and the effectiveness of destruction of VOC and CO contained in the off-gas stream.

A DuPont team has been formed to design a commercial catalytic N_2O decomposition process. One notable design factor is control of the exotherm produced when N_2O is converted to N_2 and O_2 (ca. 600°C-700°C for 30 percent N_2O). Standard engineering options available for temperature control include dilution (e.g., air or cooled recycle) or direct heat removal from the bed. The heat of N_2O decomposition can be used to generate steam. The proposed system will also utilize commercially available SCR technology for abatement of the NO_x contained in the off-gas stream. A typical flow diagram for catalytic decomposition of N_2O in adipic acid off-gases is illustrated in Figure 1.

OTHER USES FOR N_2O

During the past 40 years, many possible alternative uses have been considered for the substantial volume of N_2O produced as a byproduct in adipic acid manufacture. Sale of N_2O (laughing gas) has been considered several times in the past and rejected due to concerns about the cost of purification and unattractive economics. DuPont's supply of N_2O is many times higher than the U.S. market. N_2O has also been considered as a feedstock—for example; to carry out selective oxidation reactions. We expect to continue looking for opportunities in this area in the future.

CONCLUSIONS

Major adipic acid producers worldwide have agreed to substantially reduce N_2O emissions associated with AA manufacture by 1996–98. Producers have formed an inter-industry group to share information on technologies being developed for N_2O control. Technology options being studied by DuPont and others include advanced thermal destruction, conversion to NO for recovery, and catalytic decomposition to N_2 and O_2. The adipic acid producers expect that different N_2O abatement processes will be optimum for different sites, so that all three of the proposed technologies may ultimately be implemented. DuPont has chosen catalytic abatement as the most economical process for its North American sites, and is currently aiming to accomplish N_2O abatement at all sites by 1996.

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Soil Washing and Radioactive Contamination

Dirk Gombert

Westinghouse Idaho Nuclear Company, Inc.,
P.O. Box 4000, Idaho Falls, Idaho 83415-4000

INTRODUCTION

Soil washing, a treatment technique which may combine both physical and chemical processes to produce significant volume reduction of contaminated soils, is widely regarded as a panacea for the huge inventory of contaminated soils in the DOE Complex. While the technology has been demonstrated for organics and to some extent for metals, review of available publications on practical applications to radioactive sites indicates that most volume reduction is a product of unique circumstances such as screening or floating out non-soil materials containing most of the contaninants, or leaching contaminants (uranium or transuranic elements) that exist as anionic complexes [*1*] which are not held by the soil cation-exchange-capacity. In either case, the potential for success of the technology is extremely site and contaminant specific.

Environmental remediation techniques are based on the same principles used in mining, chemical manufacture, and water treatment. Nothing magic is implied by the environmental application; this new industry is just based on creative combinations of existing technology, with a little development to reach new goals. The constraints of waste and cost minimization have never been more critical.

This paper discusses the state of the technology and the unique challenges of treating radioactively contaminated soils, then focuses on how soil washing could be evaluated to provide definitive answers on when and where it should be employed. A logical, methodical approach must be designed to establish minimum acceptable criteria, determine what the controlling phenomena are, and then objectively evaluate whether a technology can potentially be applied to the problem. The Environmental Protection Agency's (EPA) guidance on soil washing treatability studies suggests a 50 percent reduction of contamination in particles over 2 mm as a reasonable cutoff for choosing soil washing for further development [*2*]. Once the decision has been made to attempt development, a systems approach is imperative to ensure a practical solutions. The EPA guidance also suggests a concept not so well recognized; "Residual risk, as applied to soil washing, assesses the risks associated with treatment residuals. . .sidestream and other treatment train processes should be included" [*2*]. Soil leachants cannot increase the toxicity of the soil product, interfere with downstream water treatment, or present an unacceptable hazard to remediation workers. This "big-picture" approach is frequently lost in the drive to develop the "magic bullet."

TECHNOLOGY

Mining Industry

A wealth of experience and knowledge is available in the mining industry on the recovery of metals. Commodity values have pushed retrieval efficiencies above 80 percent for ores containing parts-per-million (ppm) quantities of gold [*3*]. Crushing, screening, and grinding equipment comes in a wide variety of shapes and sizes. Particle size reduction is done to release individual mineral grains, remove surface contaminants, enhance chemical contact, and prepare material for particular applications. Though not typically viewed as a chemical engineering specialty, even Perry's Handbook devotes an entire chapter to these technologies [*4*].

Physical separation requires a distinct size or density difference between the material to be processed and the reject material. Where the species of interest exists in distinct particles, screening, settling, or flotation may be applied to provide a first cut, such that more cost-effective processing can be targeted at the more concentrated media. In some cases the particles may require separation from the host matrix or a depositional phase by grinding or attrition scrubbing. Settling and flotation may be facilitated by chemical additions that are species specific and cause or eccentuate density differences to promote settling or floating.

Acid leaching is typical of a chemical extraction to further concentrate the material for retrieval prior to purifying for its intended purpose. Acid is relatively inexpensive, and metals can be readily removed from other soluble salts, so the gross dissolution of other acid soluble compounds is acceptable. Once the metals are removed, the remaining salt bearing solution can be dried to a cake in an open evaporation pond.

Soil Washing

Application of these technologies to environmental restoration purposes entails a set of more confining constraints, while trying to satisfy more demanding goals. Not only do the contaminants include organics and inorganics, with cleanup criteria which may be orders-of-magnitude lower, but all effluents are subject to scrutiny for residual contamination. Surveys of soil washing as currently applied, particularly in Europe, show a key similarity in relying on size classification (physical soil washing) for the primary contaminant separation. Particles below a 63 to 74 micron cutoff range are separated and disposed of as hazardous waste [*5*, *6*, *7*]. Though chemical extraction may be employed in conjunction with the separation process, it is commonly accepted that fine particulate present in solution may resorb extracted contaminants, and it is not cost effective to continue to wash the fines. Soils containing more than 20 percent fines below the cutoff level, are generally not cost effectively treated with physical soil washing [*5*, *6*, *7*]. Thus soil washing typically provides volume reduction by a factor of 5–10, but does not actually reduce the toxicity of the contaminants.

While organic contamination is typically bound by the naturally occurring organic content of the soil, [*8*] or as coatings on larger particles, inorganic contaminants may be bound through any combination of several mechanisms including ion exchange, chemical and physical adsorption, precipitation, isomorphic substitution, and agglomeration. Adding to this complication is the extremely site and species specific nature of the problem. A chemical soil washing (extractive) flowsheet that works well to remove gasoline from a moist, humic soil would have a slim chance for success removing cadmium from an arid calcereous soil. Even a system proven successful for removing the same element from the same soil could have difficulty due to speciation, as is the case for trivalent versus hexavalent chromium. Applying extractive soil washing technology to inorganic removal requires a quantum leap in sophistication from the relatively simple application of heated water and surfactants which can be quite effective for organic contaminants. Even now satisfactory results beyond size classification cannot be obtained for many metals in many environments.

Radioactive Contamination

Adapting this technology to radionuclide contaminated soils presents a much greater challenge. At the Idaho National Engineering Laboratory (INEL), for example, some contaminated soils and sludges are one-third to three-quarters material below 50 micron [*9*, *10*]. In addition, the contaminants may not exist as individual particulate; being derived from aqueous solutions, many radionuclides contaminate soils on an atomic level. The contaminants are not limited to transition and heavy metals, but also include alkalies and alkaline earth fission products that are chemically analogous to natural soil constituents which make up percent levels of the soil matrix. It is obviously questionable whether soil washing is applicable to these contaminants. More questionable is the ability to reach the radionuclide cleanup goals even if the conditions are ideal.

"How clean is clean?" takes on a special significance when radionuclides are discussed because instrumentation exists to measure radioactivity to extraordinarily low levels, and the risks projected by the cancer initiation models in use by the EPA have no lower bound [*11*]. To date, below regulatory concern (BRC) levels have not been quantified. The waste disposition criteria for radionuclides in commercial landfills permitted under the Resource Conservation and Recovery Act (RCRA) have defaulted to background values, which vary by location, but are very low everywhere, particularly for fission products. Continued placement of radioactive soils in Department of Energy (DOE) controlled landfills is complicated by the frequent association of radionuclides with regulated heavy metals and organics (mixed waste). The technology exists to treat most soils to the extent that they will pass the toxic characteristic leach procedure (TCLP) criteria under RCRA, but treatment may be complicated if not precluded entirely by radioactive contamination. Chemically extracting metals to meet the TCLP requirements such that soils may be placed in landfills may leave a significant non-leachable metal content in the soil, but radionuclide limits are not simply a function of leachability. The very existence of radionuclides presents a potential cancer hazard as a function of proximity due to the non-contact effects of ionizing radiation. Obtaining contact handling standards of 5 millirem per hour for soils contaminated with cesium-137 requires contaminant reduction to parts-per-billion (ppb) levels. Treatment to eliminate all significant risks to allow free release, that is lower than the typically acceptable 10^{-6} levels under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) for remediatiion efforts, [*12*] can require decontamination down to part-per-trillion (ppt) levels in the soil [*13*]. This may require innovative extractive processing following physical separation.

Were it not for the potentially huge environmental gains to be made by successfully developing soil washing for remediating radionuclide bearing soils, the concept would have already been dropped. To develop an adequate knowledge base to definitively judge the usefulness of the technology requires some basic research in how the contaminants are bound, so flowsheets can be targeted at the controlling mechanisms. Without this knowledge, trial-and-error methods may never give the technology a comprehensive evaluation. It is very possible to free a species from one mechanism, while making it susceptible to another, with no net release from the soil. To obtain release, gross dissolution of an unnecessarily great fraction of the soil using acid may result in magnifying the waste disposal problem. Without the basic knowledge on what binds the contaminant, it may only be fortuitous to develop an acceptable strategy.

EVALUATION

Fixation Mechanisms

A logical evaluation program should begin to establish the insight necessary to either support site-specific soil washing flowsheet design or abandon the technology. As in a chemical process, where the rate-controlling step is identified so the design can fully exploit the kinetics, the key to evaluating a decontamination process is understanding how the contaminants are fixed. The strong retention of radionuclides in some soils was once considered an asset because it served as a final barrier to contamination of ground water. This attribute is now a liability to returning contaminated soils to a near pristine condition for uncontrolled release. Understanding the fixation mechanism(s) is necessary to developing an effective strategy to induce release.

Many inorganic contaminants are held in soils by physical adsorption or cation exchange due to the electrical charge on soil particles, particularly clays. Cations are attracted to the broken edges of silicate layers to stabilize the negative charge imbalance that occurs where the silica tetrahedra are incomplete. The electroneutrality may also be upset by isomorphic substitution of an ion of lesser charge. For example, a trivalent aluminum or iron ion may substitute for a tetravalent silicon ion leaving the matrix with a net negative charge [*14*]. This effect can be strongly influenced by pH; as pH is increased, the ability of water to stabilize the matrix is reduced, and the cation exchange capacity of the soil is increased [*14*]. Strontium has been shown to be less strongly bound by clays at lower pH values, probably due to reduced dissociation at hydroxyl sites, and the net positive charge induced by aluminum and iron oxides [*15*]. Similar to specialty ion exchange resins, some materials favor specific ions due to differences in relative affinity, charge spacing, or steric hinderances. Note that some contaminants exist in solution as anionic complexes or compounds and are held by analogous, but opposite forces. Some materials can be fixed in either manner depending on the soil redox chemistry and pH.

Contaminants can also be bound through precipitation from a super-saturated solution, coprecipitated with another material, or physically bound in an agglomerate due to the characteristics of another compound. As a solution evaporates, it eventually becomes super-saturated, and the salts crystallize on whatever solid surface to which they are exposed. Exposed to water again, these salts are typically redissolved, however, if they precipitate in pores where flow cannot be established, or as a new relatively insoluble compound, dissolution may be drastically limited. The local chemical equilibrium may also be controlled by pH such as in the carbon dioxide/carbonate/bicarbonate system which can cause fixation over a very sharp pH gradient around a carbonate mineral such as limestone [*16*].

Hydrated metal oxides are well known for their tendency to concentrate heavy metals. Oxides of aluminum, manganese, and iron readily hydrate to form a semi-continuous layer which may occlude other cations of particles [*17*, *14*]. Their effect may be disproportionate to their concentration in the soil because they tend to form thin coatings on particles, yielding a tremendous surface area for fixing contaminants. Chemically or physically removing these layers would generally act to the benefit of removing a contaminant, but the layer may cover or block pore spaces or ion exchange sites, and removal may open these other sites for active fixation. Though these new sites would probably fix less contamination than that fixed by the hydrated oxides, the degree of decontamination realized may be lessened by this effect.

Organic materials may also bind contaminants due to biological activity, stabilization by free organic ligands such as polyelectrolytes, or charge neutralization with organic acids [*16*, *18*]. Highly humic soils are typically acidic which tends to keep metals soluble, but also generally have a high cation exchange capacity (CEC) due to the activity of these other phenomena [*14*].

Over a long enough time contaminants may also substitute in a mineral lattice, becoming a part of the undissolved mineral fraction of the soil. Ironically, though this material is all but unavailable to the environment biologically, if radionuclides are involved, much investment may be necessary to solubilize them for removal.

Mechanism Identification

Certainly wet-screening the material to determine if a significant fraction may be discarded without treatment is a sound start. The contaminant distribution may be altered in favor of additional physical separation by controlled attrition of surface deposits. Flotation may be necesary to completely separate the fine clay and organic particles from the more coarse material. Complete segregation of size fractions is essential to evaluate contaminant distribution and the potential for physical volume reduction.

Assay of the soil fractions will not only identify which fraction(s) on which to focus, but analyses of other typical soil constituents may also provide initial insight into any correlations between the contaminants and compounds in which they could be fixed. These analyses will also provide the basis for understanding the soil chemistry, e.g. acidity, alkalinity, organic content, and fines fraction. For a small amount of soil, or a relatively straight forward decontamination, simple trial-and-error with the most widely used or most probably effective cleaning agents such as water (hot or cold), detergents, or possibly acid of caustic may be completely satisfactory to evaluate the efficacy or soil washing. For more complicated contaminants such as soil analogues, particularly with radionuclides where long term disposition and control drives waste minimization more than short-term costs, a more insightful strategy may be necessary. The more learned about the contaminant retention in the soils, the more likely an efficient contaminant-specific release flowsheet will be developed. Not all trial and error can be eliminated from the R&D program. However, developing a hypothesis on the principal retention mechanism(s) for a species in a particular matrix will provide a basis for organizing an experimental strategy.

The next step may include a surface analysis if possible. Though the contamination could penetrate into the individual particles over time, the contamination was introduced from an external source, and therefore should reside primarily on the surface. Elemental mapping of the surface with a scanning electron microscope (SEM) may corroborate correlations indicated by the chemical assays, or it may indicate less obvious correlations such as the disproportionate metal fixing capability of the hydrated metal oxide films described earlier. While electron spectroscopy for chemical analyses (ESCA) is expensive, it may give direct indication of the compounds fixing the contaminants of concern.

Though significant work has been done to quantify the relative retention characteristics of contaminants in soils, most of this research has been in support of migration modelling [*19*]. Little work has been found in the environmental literature on studies dedicated to defining how radioactive contaminants are retained. What research there is, relates to decontamination of low-level wastes (Cs^{137} and Sr^{90}) by ion exchange on clays and silico-titanates [*20*, *21*]. The function of clay is described above. The titanates are of interest because these materials can be engineered for ion-selectivity by controlling lattice spacings to function in a manner similar to molecular sieves.

Contact with many commercial vendors of soil washing technology has explained the dearth of published data; virtually all testing data with RCRA regulated species is protected as proprietary, and little or no work has been done with radionuclides because of the regulatory morass which makes profit questionable.

Much can be learned, however, from bioavailability studies on heavy metals in soils [*16*, *22*, *23*, *24*]. Sequential leaching experiments are designed to destroy one fixation mechanism at a time, progressing from relatively mild to increasingly more aggressive treatments. Chemical analyses of both the solids and the leachate between steps suggest the mode of fixation for each contaminant. The finesse is in designing a treatment that will efficiently eliminate one mechanism, without attacking the remaining matrix. Not only is this ideality impossible to fully attain, it can be masked by the refixation of the contaminants in the remaining solids. In addition to providing step-wise yield data for the contaminants of concern, the chemical analyses can help to adjust the extraction procedure by providing verification of how completely a mechanistic compound is removed, and some insight into the unavoidable attack on the remaining mechanisms. Though imperfect, this technique can be used to deduce the most probable fixation mechanism so that it may be targeted by a flowsheet.

Table 1 summarizes some of the reagents listed in the references cited above to perform selective leach experiments. This is by no means a comprehensive list, and reference to the original publications and bibliographies contained therein is recommended for evaluating which treatment is most applicable to a given soil. The leachants are listed by mechanism/phase attacked, in the order of the typical sequential design. The first leach should be dedicated to physical adsorbtion and ion exchange, the second, carbonates, etc.

Examples of some of the leachant limitations and experimental suggestions gleaned from the literature are as follows:

Some of the ion exchange solutions may also attack calcium carbonate either due to the acetate complexing the calcium, or the ammonium ion neutralizing the carbonate [*16*]. Running the extraction at slightly over pH 8 rather than in a neutral solution may mitigate the complexing effect, and using the sodium salt may eliminate the neutralization problem [*16*]. In addition to pH, the time and temperature of the extraction should be held constant, experiment to experiment, to minimize data variability [*16*].

Reducible metal fractions may be altered during sample preparation, such as exposure to air for samples from reducing environments [*16*]. Chelating, and complexing effects of leach

Table 1 Mechanism Specific Leachants

Target Mechanism	Leachant
Adsorption/Ion exchange	0.05 M $CaCl_2$ $BaCl_2$, Triethanolamine, pH 8.1 $MgCl_2$, pH 7 NH_4OAc, pH 7, 8.2 NaOAc
Carbonates	CO_2 NaOAc/HOAc buffer, pH 5
Reducible Oxides	Acidic Hydroxylamine in Ammonium-Oxalate Buffer Hydroxylamine/Acetic acid 0.1 M NH_2OH/HCl, 0.01 M HNO_3, pH 2 0.2 M Ammonium Oxalate, 0.2 M oxalic acid, pH 3 Ammonium Oxalate/Oxalic Acid with UV Sodium Dithionite-Citrate Buffer Hydroxylamine/HCl, Acetic Acid
Organic/Sulfides	H_2O_2, NH_4OAc, pH 2.5 30% H_2O_2, 0.02 M HNO_3, pH 2, 85°C Organic Solvents 0.1 M NaOH, H_2SO_4 Potassium pyrophosphate
Residual	HNO_3 (conc.), 180°C Aqua Regia, HF, Boric acid $HF/HClO_4$

solution anions may also yield confusing results for metals [*16*]. Reprecipitation may occur due to pH swings at particle interfaces, or in the solution due to loss/gain of carbon dioxide [*16*]. Adjusting the pH up to 3, and decreasing the contact time to 15 minutes and the reagent concentration to 0.025 M may make the hydroxylamine hydrochloride leachant even more specific, removing the more readily reduced manganese oxides while leaving the iron oxides virtually intact [*25*].

Using sulfide bearing reagents may cause low solubility metal-sulfides to be lost from solution [*16*]. Care should also be taken in using dithionite because of inherent zinc contamination, and residual extractant can cause plugging problems in atomic absorption equipment [*23*].

Sodium and potassium chlorides have also been used to displace strontium and cesium [*26*]. Calcium chloride was shown to effective displace strontium which might be expected from their chemical similarity, but potassium seemed to be far more effective at displacing cesium than was sodium [*27*]. This may be due to the relative natural affinities predicted in the Hofmeister Series [*28*], or some degree of steric hinderance as in the case of a molecular sieve.

Chelants have also been used to extract heavy metals from soils [*29*], but are notably absent from Table 1. These materials enhance solubility, but provide no mechanism specific attack, and therefore are not particularly effective for a sequential leach.

The spacial variability of soils cannot be overstated. Just as each mechanistic study is unique to the location and contaminants, multiple samples from the same site may vary enough to mask trends in experimental data. Care must be taken to eliminate unique characteristics between samples. Adequate blending of the initial source material for experiments to ensure homogeneity is essential.

CONCLUSIONS

There is no question that there is a need for R&D to minimize the amount of waste the DOE must control for years to come. Though trial-and-error testing is quick and relatively inexpensive, it provides little or no insight for technology transfer to other locations. A mechanistic approach yields enough data to help explain how a process works or why it should not be considered further. With this level of understanding, it will be easier to defend the evaluation as comprehensive to local communities. Finally, developing flowsheets to minimize waste, by minimizing the amount of soil dissolved, is cost effective.

Timely treatability studies are necessary to evaluate the potential for technologies such as soil washing for application to readionuclide contamination. The goal of the research should be to provide adequate insight into the physical/chemical processes involved to determine if soil washing should be considered for remedial action with radioactive soils. Soil assays, surface analyses, and sequential leaching strategies are tools available to provide the knowledge base needed to make informed decisions. Hopefully, the recommendation to the public to drop, selectively apply, or regard soil washing as a true "magic bullet" will be based on science.

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Use of Electrochemical Iron Generation for Removing Heavy Metals from Contaminated Groundwater

M. D. Brewster and R. J. Passmore
Andco Environmental Processes, Inc., Buffalo, NY 14228-2380

This paper utilizes data from two pilot studies conducted at Superfund Sites to discuss the electrochemical iron addition process developed by Andco Environmental Processes, Inc. Electrical current and steel electrodes were used to put ferrous and hydroxyl ions into solution. Once added, the chemistry was properly manipulated to provide coprecipitation and adsorption conditions capable of simultaneously removing a wide variety of heavy metals. The goals of the two projects were distinctly different. At the first site, conversion of ferrous ions to the ferric state resulted in thorough reduction of hexavalent chromium to trivalent chromium. Observations and results from this study are used to discuss system design, sludge production, and operating costs. At the second location, high concentrations of many metals required removal. The presence of arsenic necessitated chemically induced oxidation. Hydrogen peroxide was introduced to convert Fe^{+2} to Fe^{+3} and arsenite to arsenate. By efficiently shifting the equilibrium state and adjusting pH to create conditions for maximum anion adsorption, an arsenic removal efficiency of over 99.8 percent was obtained. Proper process application resulted in simultaneous removal of aluminum, arsenic, cadmium, chromium, lead, mercury, nickel, selenium, thallium, and zinc. Also, when necessary treatment conditions were provided and maintained, metals removal by three major mechanisms resulted in iron matrices that passed regulatory levels listed in conjunction with the Toxicity Characteristic Leaching Procedures (TCLP).

INTRODUCTION

At most superfund sites, many heavy metals must be removed from contaminated groundwater. Simultaneous extraction is complicated due to the various chemical properties that metals exhibit. A comprehensive understanding of solubilities, oxidation states, and adsorptive mechanisms is needed to accomplish treatment objectives. The means by which a treatment process is implemented often affects oxidation-reduction conditions and removal mechanisms such as precipitation, surface complexation, and electrostatic attraction. Two recently completed pilot studies using freshly generated and highly active ferrous ions are ideal for explaining metals removal mechanisms. They also provide valuable suggestions regarding application of oxidation and/or reduction conditions and implementation of full-scale pump and treat groundwater remediation systems.

Pilot Study 1 was conducted at the Palmetto Wood Pre-

M. D. Brewster is presently employed at Argonne National Laboratory, Argonne, IL 60439.

serving Superfund Site located in Cayce, South Carolina. As the result of many years of wood preservation operations and improper handling of excess preservatives, the groundwater was contaminated with hexavalent chromium. To evaluate Andco's electrochemical iron generation process, samples prior to and following treatment were analyzed for aluminum, arsenic, barium, total chromium, hexavalent chromium, copper, lead, and mercury. Pilot Study 2 was done at the Dublin Road Landfill Superfund Site located in the towns of Ridgeway and Shelby, New York. For this study, electrochemical iron addition and chemical oxidation were required for thorough arsenic removal. To evaluate process efficiency, influent and effluent samples were analyzed for cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc.

REMOVAL MECHANISMS

Wastewater treatment terminology often includes adsorption, coprecipitation, surface complexation, and electrostatic attraction. Frequently the processes overlap and distinction becomes difficult. For sake of this discussion and to describe why the proposed treatment scheme works, two simple terms will be described; precipitation and adsorption. Adsorption includes surface complexation and electrostatic attraction. Since successful hexavalent chromium treatment requires chemical reduction, iron induced chromium reduction will also be discussed.

Precipitation

The most common method for removing dissolved metal ions from solution is to add the counter ion needed to form an insoluble precipitate. For example, many heavy metals are precipitated as metal hydroxides or metal sulfides by addition of hydroxide or sulfide ions. Figure 1 contains solubility curves for precipitation of cadmium hydroxide, lead hydroxide, chromium hydroxide, and copper hydroxide. It is important to note that chromium's and lead's points of minimum solubility are greater than presently enforced drinking water standards. As of May 1990, the Environmental Protection Agency (EPA) Maximum Contaminant Levels (MCL) allows for point source discharges of chromium and lead are 0.1 and 0.015 milligrams per liter, respectively [*1*].

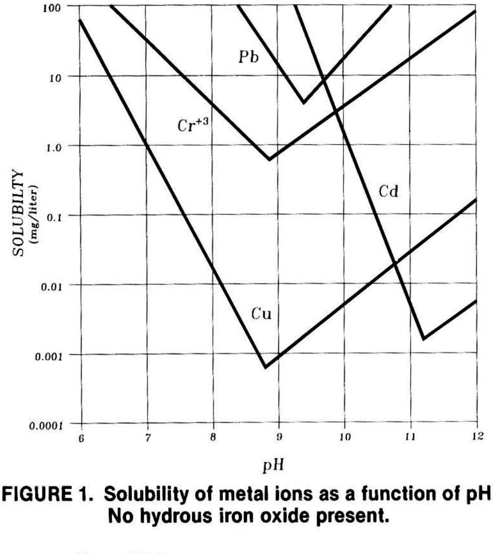

FIGURE 1. Solubility of metal ions as a function of pH. No hydrous iron oxide present.

Depending on the initial concentration and form of arsenic, precipitation is a viable and effective first step in the treatment scheme. It has been shown that iron (Fe^{+3}) readily precipitates ferric arsenate but not an insoluble iron arsenite. At ambient temperature, the minimum solubility of iron arsenate allows a significant amount (7.5 mg/liter) of arsenic to remain in solution [*2*]. Thus, if arsenic is present at concentrations above 7.5 mg/liter and correct pH conditions exist, precipitation of ferric arsenate will occur. To achieve arsenic residuals like those reported in this paper, removal by adsorptive mechanisms must be considered and promoted.

Chromium Reduction

When considering hexavalent chromium, as chromate (CrO_4^{-2}), a few insoluble chromate containing precipitates are known but it is not practical to add barium or lead as a treatment chemical. Chromate removal usually lies on chemical reduction to convert highly toxic and soluble hexavalent chromium to the less toxic and virtually insoluble trivalent form. Experimental results of Eary and Rai indicated that the most efficient method of chromium reduction was the introduction of iron ions as ferrous salts [*3*]. They also concluded that reaction stoichiometry was maintained over the broad pH range of 2-10. Most chromium contaminated process water and groundwater is within that pH range. Compared to other chromium reduction technologies, iron based chromium treatment requires no initial pH adjustment step. Many methods of chromium reduction are available but the preferred one is to use electrochemically generated ferrous ions to convert Cr^{+6} to Cr^{+3} while being oxidized to the ferric state. Due to the oxidation-reduction potential relationship between ferrous iron and hexavalent chromium, near instantaneous oxidation of iron and reduction of chromium occur as ferrous ions enter solution in the electrochemical cell. The overall reaction is as follows:

$$CrO_4^{-2} + 3Fe^{+2} + 4H_2O \rightarrow Cr^{+3} + 3Fe^{+3} + 8OH^-$$

The method is preferred mainly because hydroxyl ions are generated along with the iron ions. Very little pH change results. Thus, the need for pH adjustment chemicals is minimized. Having hydrous iron oxide present has an additional benefit. Through formation of a chromium containing hydrous iron oxide complex precipitate [*3*] and adsorption (surface complexation and electrostatic attraction), very low metals residuals are achieved. Figure 2 has been provided to illustrate

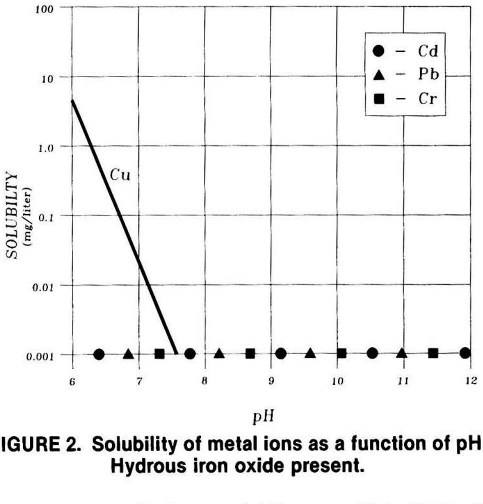

FIGURE 2. Solubility of metal ions as a function of pH. Hydrous iron oxide present.

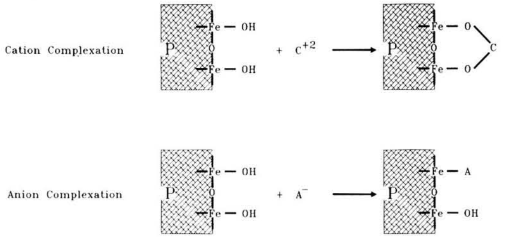

FIGURE 3. Surface complexation on hydrous iron oxide. P = interior of suspended particle.

how solubility curves are flattened and broadened when adsorption on hydrous iron oxide is promoted.

Compared to performing treatment with ferrous sulfate or ferric chloride, electrochemical iron generation has several distinct advantages. Iron introduced without corresponding sulfate or chloride ions is more efficient at removing contaminants from aqueous streams. By eliminating competing anions and using a highly pure iron source, lower metals residuals are obtained and less sludge is produced than when iron salts are utilized. A contaminant free iron source allows maximum adsorptive removal of the various dissolved forms of metals that could be present and require treatment. Iron salts significantly increase total dissolved solids (TDS). If little or no pH adjustment is needed, iron added electrochemically will reduce TDS. Contaminants present in industrial grade ferrous sulfate and ferric chloride end up in either the treated effluent or sludge cake. If flow rates or contaminant loads fluctuate, chemical treatment systems are difficult to operate. By turning a dial, electrochemical iron dosing is controlled. This provides maximum flexibility and thorough system optimization. The electrochemical process is easily adjusted for sludge minimization while still meeting all discharge criteria.

Adsorption

Adsorption has been identified as a viable removal mechanism. Surface complexation and electrostatic attraction are the two most commonly used adsorption terms. Heavy metal contaminants can exist as either cations (i.e., Cr^{+3}) or anions (i.e., CrO_4^{-2} and AsO_4^{-3}). A schematic representation of surface complex formation on a suspended particle of hydrous iron oxide is given in Figure 3 [*5*]. After forming all possible surface complexes, it is possible to remove contaminants by simple electrostatic attractions. Hydrous ferric oxide in combination with various surface complexes contains areas of apparent positive and negative charges. Opposite charges attract and are strong enough to remove some dissolved species from the aqueous phase.

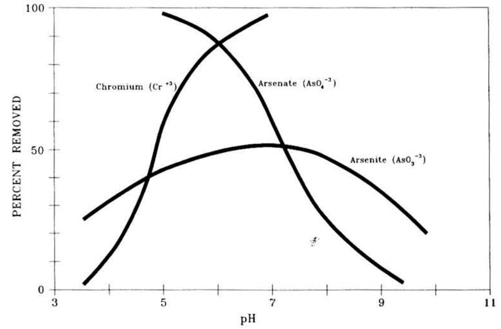

FIGURE 4. Adsorption on hydrous iron oxide.

The two most important factors to consider when adsorptive removal of heavy metals is desired are pH and the hydrous iron oxide to contaminant weight ratio. If adequate adsorbing matrix is provided for complete adsorption, pH control is critical. In Figure 4, typical adsorption curves for chromium, arsenate, and arsenite have been provided [*6*]. Adsorption of cations improves as pH is increased. The arsenate curve is typical for anions with removal improving as pH is decreased. An arsenite curve was included to support the need for chemical oxidation from arsenite to arsenate, to enhance removal via adsorption on hydrous ferric oxide.

PILOT STUDY DESCRIPTIONS

Andco's process, shown in Figure 5, utilizes an electrochemical cell to generate hydrous iron oxide directly from steel electrodes. In a full-scale system, process water is first pumped through the electrochemical cell. The electrochemical cell consists of a fiberglass body containing a number of cold rolled steel plates, which act as electrodes. Inside the cell, the electrodes are separated by a small gap. The wastewater flows through the gaps in contact with the electrodes. A DC power supply is connected between the cell's two end electrodes. As current flows from electrode to electrode through the process water, an electrochemical reaction occurs where the positively charged sides, the anodes, of the electrode give off ferrous ions. Iron addition is controlled simply by varying the cell power. At the negative sides, the cathodes, water breaks down into hydrogen gas and hydroxyl ions. The overall reaction results in the formation of ferrous hydroxide. As iron hydroxide is generated, the electrodes are slowly consumed. The generated ferrous ions react with hexavalent chromium to form ferric ions and trivalent chromium. At this point, treatment differs for Pilot Study 1 and Pilot Study 2.

Pilot Study 1

For Pilot Study 1, after exiting the electrochemical cell the process water flows to a retention tank. In the retention tank, a small amount of air may be required to oxidize any remaining ferrous hydroxide to ferric hydroxide. In most cases, no air is needed because the dissolved oxygen content of the process water will oxidize the residual ferrous iron to the ferric form. The water gravity flows to a reactor. The reactor tank has a pH probe and pH controller to ensure optimal pH for precipitation of the iron and chromium.

Pilot Study 2

For Pilot Study 2 water exiting the electrochemical cell flows to a reactor tank. In the reactor tank, hydrogen peroxide is

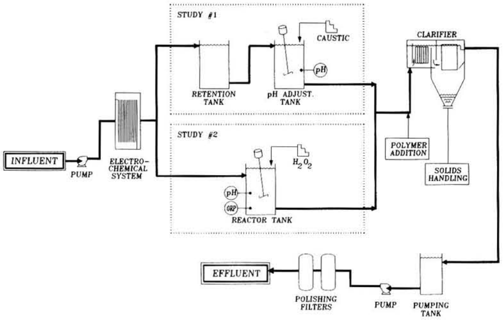

FIGURE 5. Process flow diagram.

Table 1 South Carolina Wood Preserving Site Results. Electrochemical Iron Dosage = 20 mg/l.

	Treatment System Performance				
Parameter	Influent mg/l	Effluent mg/l	Discharge Limits mg/l	TCLP Results mg/l	TCLP Limits mg/l
Aluminum	0.10	<0.05	35.0	——	——
Arsenic	<0.005	<0.005	0.02	<0.005	5.0
Barium	0.23	<0.005	——	4.0	100.0
Cadmium	——	——	——	<0.01	1.0
Chromium	3.5	<0.05	2.0	<0.05	5.0
Chromium (+6)	3.3	<0.05	0.05	——	——
Copper	<0.05	<0.05	1.0	——	——
Lead	<0.005	<0.005	0.03	<0.005	5.0
Mercury	<0.0002	<0.0002	——	<0.0002	0.2
Selenium	——	——	——	<0.0005	1.0
Silver	——	——	——	<0.05	5.0

added based on a signal from an oxidation reduction potential (ORP) probe. Hydrogen peroxide addition oxidizes the ferrous hydroxide to the ferric form, and also serves to oxidize any portion of the arsenic which is in the arsenite state to the arsenate state. The reactor tank has a pH probe and controller to assure an optimum precipitation pH.

From the reactor tanks of both studies, the process water flows to a clarifier. Before entering the clarifier, a small amount of polymer flocculent is added to improve the settling properties of the precipitated solids. Newly formed solids settle to the bottom of the clarifier while the overflow flows to a polishing filter before exiting the system. Settled solids are typically sent to a plate and frame type filter press for dewatering. Content of the filter cake collected at the Cayce, South Carolina site (Pilot Study 1) will consist of hydrous ferric oxide, a chromium containing iron hydroxide complex, chromium hydroxide, and any other suspended solids or metals removed by the process. Sludge generated at the Superfund Site located in New York (Pilot Study 2) will contain hydrous ferric oxide, ferric arsenate, hydrous ferric oxide/arsenic complexes, and other contaminants simultaneously removed during treatment.

RESULTS AND DISCUSSION

Pilot Study 1

Pilot Study 1 performed at the Superfund Site located in Cayce, South Carolina used a twenty gallon per minute flow through electrochemical cell in combination with slight pH adjustment, polymer assisted clarification, and multi-media filtration. The treatment process, as diagrammed in Figure 5, was assembled on a trailer and transported to the site.

Influent conditions for the groundwater at the site are provided in Table 1. Based on metals concentrations, an electrochemical iron dosage and clarification pH were chosen that would assure complete chromium reduction, maximum adsorption, and excellent clarification. Samples were collected at various stages of the treatment process and analyzed for the heavy metals of concern. Following collection, samples were properly preserved and sent to an EPA certified laboratory. Results show that after clarification and filtration, metals residuals were less than analytical detection and several times less than discharge limits for the site [7]. Besides chromium, only barium and aluminum were detected in the untreated groundwater. Since concentrations of each were near or below points of minimum solubility, it was concluded that removal occurred via adsorption.

As part of this study, filter cake was collected and sent to the EPA approved laboratory in order to perform a Toxicity Characteristic Leaching Procedure (TCLP) analysis. The TCLP test quantifies amounts of metals disassociated from the solid phase when subjected to passage of a dilute acid solution. If leachable metals are below prescribed EPA permissible concentrations, the filter cake is deemed non-hazardous and allowed to be sent to a non-hazardous landfill for disposal. The results of the TCLP test are also given in Table 1. As can be seen, the filter cake passed the TCLP test. This confirms how tightly the contaminants are bound in the electrochemically generated iron matrix. Barium's presence in the TCLP extract

Table 2 Chemical Consumptions and Operating Costs. Pilot Plant Treated 28,336 Gallons.

Parameter	Form	Purpose	Consumption	Unit Cost	Cost/1000 Gals
Iron	Steel Electrodes	Iron Generation	6.0 lbs	$0.39/lb	$0.08
Base	50% NaOH	pH Control	11.2 lbs	$0.095/lb	$0.04
Acid	35% HCl	Acid Wash	9.7 lbs	$0.12/lb	$0.04
Polymer	Anionic Emulsion	Flocculent	0.3 lbs	$2.90/lb	$0.03
Cell Power	——	——	28 kwh	$0.06/kwh	$0.06
Pumping and Control Power	——	——	34 kwh	$0.06/kwh	$0.07
				Total	$0.32

Table 3 Dublin Road Landfill Superfund Site Results. Electrochemical Iron Dosage = 250 mg/l.

	Treatment System Performance				
Parameter	Influent mg/l	Effluent mg/l	Discharge Limits mg/l	TCLP Results mg/l	TCLP Limits mg/l
Arsenic	54.5	0.098	0.190	<0.5	5.0
Cadmium	0.26	<0.005	——	<0.1	1.0
Chromium	0.710	<0.01	——	<0.5	5.0
Copper	0.055	<0.02	0.05	——	——
Lead	0.24	<0.005	0.009	<0.5	5.0
Mercury	0.00024	<0.0002	0.0002	<0.02	0.2
Nickel	0.415	0.024	——	——	——
Selenium	16.0	<0.025	——	<0.5	1.0
Silver	<0.01	<0.01	——	<0.5	6.0
Thallium	0.032	<0.005	——	——	——
Zinc	12.0	<0.01	——	——	——

supports the theory that removal of barium from the aqueous phase occurs through weak electrostatic removal mechanisms.

Table 2 illustrates the economics associated with treating groundwater using a system that implements electrochemical iron generation. In addition to successful metals removal and low sludge production (1.36 lb/1000 gallons treated), the system is also inexpensive to operate. Total operating cost for groundwater remediation at the Superfund Site located at Cayce, South Carolina was calculated to be $0.32 per thousand gallons of water treated.

Pilot Study 2

Electrochemical iron addition is an excellent means of simultaneously removing heavy metals from contaminated process water or groundwater. Proper process implementation allows chromium reduction and arsenic oxidation to be performed in different steps of the same treatment system without sacrificing removal efficiency of either chromium or arsenic [*8*]. Table 3 contains metals concentrations prior to and after treatment of groundwater at the Superfund Site located in New York. Based on influent concentrations (mainly arsenic), electrochemical iron and hydrogen peroxide addition rates were chosen. The one gallon per minute treatment system utilized for Pilot Study 2 is also found in Figure 5. By including both Pilot Study 1 and Pilot Study 2 in Figure 5, it is shown how chemistry is controlled and the simplicity involved in adapting electrochemical iron addition to remove a wide variety of heavy metals.

Data in Table 3 indicates that arsenic, copper, lead, and mercury can be removed to below applicable discharge limits. If all arsenic was present as inorganic forms, arsenite and arsenate, the final arsenic residual would be below 0.005 mg/liter [*9*]. It is documented that some arsenic containing pesticides were dumped at the site. Organo-arsenic compounds have less affinity for the hydrous iron oxide and thus hinder removal. Since the final arsenic concentration was below the stated discharge limit, no steps were taken to further reduce arsenic residuals. To increase arsenic removal, oxidative degradation of organo-arsenic compounds or adsorption on granular activated carbon (GAC) could have been investigated. Along with removal of four regulated metals, the process was also successful at treating cadmium, chromium, nickel, selenium, thallium, and zinc.

Sludge from Pilot Study 2 was collected and subjected to TCLP testing. No heavy metals were detected in the TCLP leachate. This indicates that removal is occurring by precipitation and surface complexation and confirms how well contaminants are incorporated into the iron matrix provided by electrochemical iron generation. This ability to form a highly stable and non-hazardous sludge is a distinct advantage of the electrochemical process over other types of precipitation schemes. All results from Pilot Study 2 have been incorporated into the client's RI/FS report to the state regulatory agency for approval to perform the groundwater remediation.

CONCLUSIONS

For Pilot Study 1, electrochemical iron generation was used for chromium reduction and combined with pH adjustment, polymer assisted clarification, and multi-media filtration for removal of aluminum, barium, and chromium to less than detection limits utilized by the analytical lab. Total chromium was removed to forty times below the site's discharge limit (Table 1). Hexavalent and total chromium removal was to below 0.05 milligrams per liter. The system was economical to operate (Table 2) and produced only a small amount of non-hazardous sludge for disposal (1.36 lb/1000 gallons treated).

To the process described and implemented in Pilot Study 1, a slight modification was needed to convert the system to an arsenic removal process (Pilot Study 2). The addition of a chemical oxidation step allowed the process to simultaneously remove ten heavy metals (Table 3) and result in a sludge cake able to pass the TCLP test due to coprecipitation and the formation of strong surface complexes.

The simple electrochemical process uses iron generation for chromium reduction and as a source of highly adsorbent hydrous iron oxide. In combination with conventional unit operations such as clarification and filtration, the process can be used for simultaneously removing many heavy metals from contaminated water. Depending on the contaminants, it is important to consider chemical oxidation and pH at which clarification is conducted. Aqueous forms of contaminants and oxidation states can be manipulated to allow complete extraction. Once clarification pH is identified, anionic polymer flocculent is effective in producing fast settling, coarse, hydrous iron oxide flocs. A final polishing step such as multi-media filtration is recommended to remove residual suspended solids and achieve the system's best performance.

ACKNOWLEDGMENTS

The authors thank Mark Allen of Bechtel Environmental, Inc., John Walsh of PEER Consultants, and Bob Aal for their cooperation and assistance. The outstanding analytical support provided by Ecology & Environmental, Inc., and James H. Carr & Associates, Inc. was also greatly appreciated.

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Cleaning of Flue Gas From Solid Waste Incinerator Plants by Wet/Semi-Dry Process

E. v. Deuster and A. Mensing
NOELL-KRC, P.O. Box 8700, Wurzburg, Germany

M. X. Jiang and H. Majdeski
NOELL, Inc., 2411 Dulles Corner Park, Herndon, VA 22071 USA

To meet the high demands on the emission limits required by German environmental regulations, well known wet absorption technology using limestone as reagent has been developed and used for specific application in municipal solid waste incineration. This system integrates two independent absorption sections in a single tower, each operating at a different pH. The process ensures the highest removal rate of harmful gases (HCl, SO_2, SO_3, HF), particulate, and vaporous fumes of heavy metals from the incineration process. The paper discusses the advantages of the wet process.

An improvement on this work has been the development of a combined technology incorporating the advantages of spray dryer and wet scrubbing. This combined technology includes a spray dryer, followed by a suitable particulate collection device, and then by the wet scrubbing stage. The purge stream from the wet scrubbing tower is returned as feed to the spray dryer. The by-product from the combination process is a completely dry powder. As a result, the need for waste water treatment for the wet scrubber purge stream is eliminated. In addition, the combination system allows low cost limestone to be used as a sorbent while providing an easy to handle, free flowing solid by-product.

This paper describes the details of the system process chemistry, criteria of the gas/liquid mass transfer, and presents the results obtained from pilot plants and commercial plants using these alternative processes.

INTRODUCTION

Incineration is a widely used method for solving waste disposal problems. However, the incineration of waste creates several noxious gases, including sulfur dioxide, hydrogen chloride, hydrogen fluoride, and vaporous fumes of heavy metals. In addition, unacceptable levels of dioxins and furans may also be generated by improper incinerator design and operation. Depending on concentrations, these gases and heavy metals can be detrimental to human health and the environment.

To comply with the ever increasing regulation requirements on the quality of cleaning flue gas in Europe, Noell offers three different well-proven flue gas cleaning processes for the abatement of noxious gases from the flue gas of waste incinerators. These processes include:

a) the spray dryer absorption process,
b) the wet scrubbing process, and
c) the combined spray dryer absorption/wet scrubbing process—the Noell combined process.

This paper briefly describes these flue gas cleaning processes, and presents the operating data and experience from pilot and commercial plants.

SPRAY DRYER ABSORPTION PROCESS

The spray dryer absorption process, showing in Figure 1, has been a reliable process for many years and is successful in the removal of sulfur dioxide as well as HCl and HF from power plant flue gas for low and medium sulfur coal with moderate consumption of energy and absorbent [*1*].

In this process, a slurry consisting of water and hydrated lime ($Ca(OH)_2$) is atomized. Atomization can be accomplished using a rotating disc atomizer, or air atomized spray nozzles. The atomized slurry droplets are brought into contact with hot flue gas in a spray drying absorption chamber. The atomized fine droplets simultaneously undergo three mass and heat transfer processes, which are:

a) mass transfer of acid gases from the gas stream into the droplets,
b) chemical reaction between acids and the dissolved $Ca(OH)_2$, and
c) evaporation of the water in the droplet.

The following overall chemical reactions take place:

$$SO_2 + Ca(OH)_2 + H_2O \rightarrow CaSO_3 \cdot \frac{1}{2} H_2O + \frac{3}{2} H_2O \qquad (1)$$

$$CaSO_3 \cdot \frac{1}{2} H_2O + \frac{1}{2} O_2 + \frac{3}{2} H_2O \rightarrow CaSO_4 \cdot 2H_2O \qquad (2)$$

$$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O \qquad (3)$$

$$2HF + Ca(OH)_2 \rightarrow CaF_2 + 2H_2O \qquad (4)$$

These chemical reactions taking place at the gas-liquid interface are instantaneous in the slurry droplets. The rates of SO_2, HCl, and HF removal are mainly dependent on the rate of the mass transfer of HF, HCl, and SO_2 through the gas film in the constant drying period, and the diffusion of acid gases through the product layer formed during processing in the falling rate drying period.

The product formed in the drying process is removed with the fly ash as a free-flowing powder in the bottom of the spray chamber and in a dust collector downstream of the spray dryer absorber. Some additional removal of noxious gases also occurs as the flue gas passes through the dust collector as a result of reaction with unreacted lime. Figure 2 shows the SEM pictures of a typical spray absorption product from an operating plant. Other vapor-phase toxic compounds can also be condensed or adsorbed on the dried dust particles.

The approach to saturation temperature has a strong effect on the spray absorption process [*2*, *3*]. The approach to saturation temperature is the difference between the exit dry-bulb temperature of the flue gas and its saturation temperature. The closer to the saturation temperature, the higher the acid gas removal. Because of the large amount of HCl present in the incineration flue gas, an excessively low approach to saturation temperature may cause serious deposition and solids handling problem. HCl in the flue gas reacts with $Ca(OH)_2$ to form calcium chloride ($CaCl_2$). Due to the hygroscopic nature of calcium chloride, adequate drying of these particles is difficult at low approaches to saturation. These particles in the gas stream may agglomerate to form a deposit layers on the vessel and the duct wall if not adequately dried. Figure 3 illustrates two different deposit layers formed during the operation. Figure 3a shows the layer structure of the fresh deposit, and Figure 3b shows the two different layers in detail. The analysis of the two layers differs only in higher chloride contents in the dark layer (see Figure 4).

In addition, the hygroscopic nature of $CaCl_2$ reduces the vapor pressure of water at the droplet interface, which, in turn can result in a decrease in the drying efficiency. Therefore, to ensure the desired removal rate of noxious gases and adequate droplets drying in the case of incineration flue gas, the retention time of the slurry droplets in the absorber is in the range of 15 to 25 seconds, and the dry-bulb temperature of the clean gas must be maintained relatively high. The configuration of the spray absorber is designed in such a way to prevent the wet particles from coming in contact with the vessel wall, thus avoiding solids deposition and corrosion.

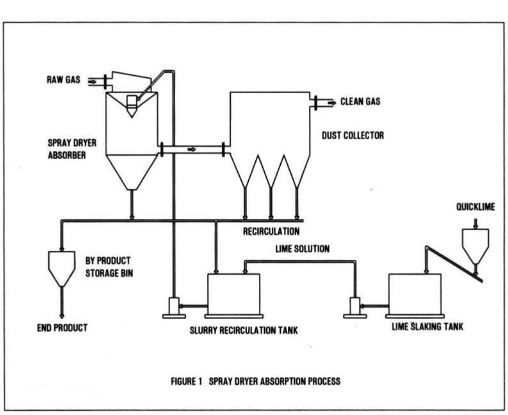
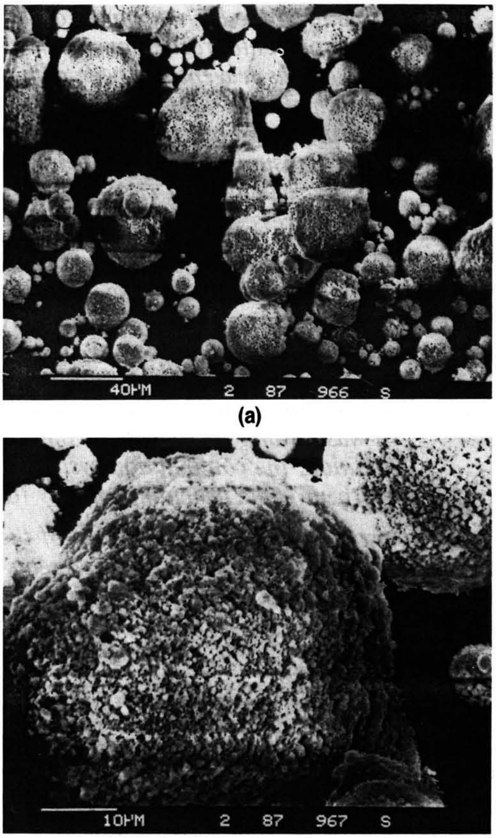


FIGURE 1. Spray dryer absorption process.



(a)

(b)

FIGURE 2. SEM pictures of typical spray dryer absorber by-product
a) Scale: 40 μm; b) Scale 10 μm.

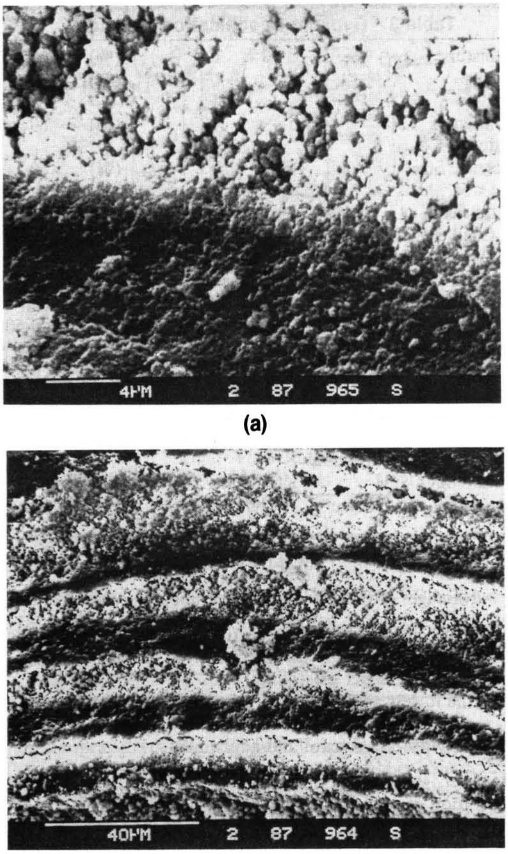


FIGURE 3. SEM pictures of spray dryer absorber deposit a) Fresh deposit; b) High chloride content deposit.

If it is acceptable to dispose of solids products from this process without further processing, or simply mixing with fly ash, then the spray dryer absorption process is an effective choice. The main advantage of this process is its dry by-product with no waste water being produced. However the utilization of a high cost sorbent, $Ca(OH)_2$, is relatively low. Table 1 lists typical noxious gases removal efficiencies using the spray absorption process under good operating conditions. The relatively low removal efficiency for SO_2 is notable.

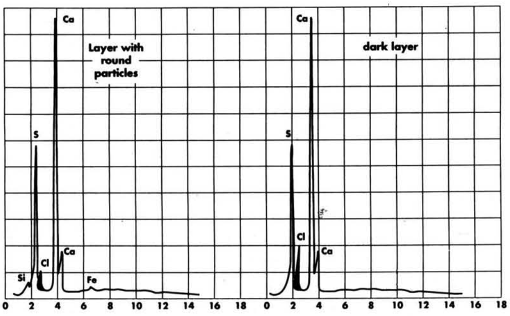


FIGURE 4. EMA results of spray dryer absorber deposit.

Table 1 Removal Efficiencies by Spray Dryer Absorption Process

Item	Units	Raw Gas	Clean Gas	Removal eff. (%)
HCl	mg/Nm^3 (dry)	845	16.5	98
SO_2	mg/Nm^3 (dry)	195	57	71
HF	mg/Nm^3 (dry)	8.7	<0.3	96
DUST	mg/Nm^3 (dry)	3300	<0.5	99.8
Pb + Zn	mg/Nm^3 (dry)	92	0.5	99.5
Cd	mg/Nm^3 (dry)	1.25	0.01	99.2
Hg	mg/Nm^3 (dry)	0.325	0.035	89.2

NOELL WET SCRUBBING PROCESS

The second alternative process is the Noell wet scrubbing process (Figure 5). This wet scrubbing process with limestone slurry was originally developed for application in high efficiency desulfurization of flue gas from power plants. It has successfully demonstrated its high reliability and economy of operation [*4*].

The Noell process is a two stage (or double-loop) process with each stage operating at a distinctly different pH level. In this process, fresh limestone slurry can be fed either to the loop alone or to both the upper and lower loop. The scrubbing slurry which contains limestone and formed by-product is sprayed into both loops with an overall stoichiometric ratio of slightly above 1.0. The flue gas enters the lower part of the scrubber (Quencher loop) tangentially and is quenched to the flue gas saturation temperature. The slurry in this loop consists of overflow from the upper loop limestone slurry feed tank. For SO_2, the overall reaction occurring in the liquid phase of the quencher slurry has the form:

$$2SO_2 + CaCO_3/CaSO_3\cdot\frac{1}{2}H_2O + O_2 + \frac{7}{2}H_2O \rightarrow 2CaSO_4\cdot 2H_2O + CO_2 + SO_2 \qquad (5)$$

with the following buffer reaction to maintain the slurry pH in the range of 4 to 5:

$$SO_2 + CaSO_3\cdot\frac{1}{2}H_2O + \frac{1}{2}H_2O \rightleftharpoons Ca(HSO_3)_2 \qquad (6)$$

The sulfite crystals mostly formed in the upper loop are dissolved with excess absorbed SO_2 in the liquid to form more soluble hydrogen sulphite. At the same time, the limestone which has been transferred in the slurry from the upper loop and has not yet reacted is converted to calcium sulfite and calcium chloride or calcium fluoride. Air is blown into the

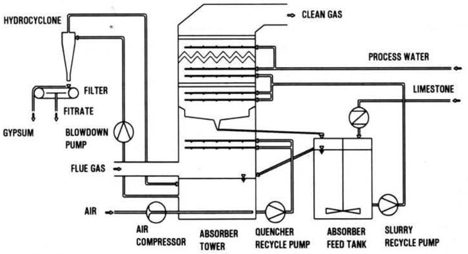


FIGURE 5. Noell wet scrubber process.

slurry sump to oxidize the dissolved calcium sulfite to form the final product—calcium sulfate crystals (gypsum).

HCl and HF gases in the flue gas are almost completely removed in the quencher loop via equations (3) and (4) mentioned previously. By this method the corrosive chlorides are limited to only a portion in this part of the scrubber.

As shown in equation (6), the calcium hydrogen sulfite formed in the liquid phase is very effective as a buffer. The pH value in the quencher slurry is almost constant irrespective of fluctuations in SO_2 concentration in the flue gas.

Exiting the quencher, the flue gas passes through the annular space around the bowl, and enters the upper spray zone above the bowl (the second loop). The bowl separates the quencher loop from upper loop by collecting the slurry from the upper loop. The flue gas is scrubbed in the upper loop to achieve the best possible removal of the remaining SO_2 in the flue gas. The liquid to gas ratio is maintained sufficiently high to provide enough mass transfer area for high SO_2 removal. The overall chemical reactions in the upper loop would have the following form:

$$2CaCO_3 + SO_2 + \frac{1}{2}H_2O \rightarrow CaCO_3/CaSO_3 \cdot \frac{1}{2}H_2O + CO_2 \quad (7)$$

$$2CaCO_3 + SO_2 + 3/2H_2O \rightarrow Ca(HCO_3)_2 + CaSO_3 \cdot \frac{1}{2}H_2O \quad (8)$$

Dissolved SO_2 reacts with dissolved limestone in the slurry to form calcium sulfite. Calcium hydrogen carbonate produced during the reaction has a good buffer effect in the upper loop slurry. The pH value is automatically adjusted by the buffer in the range of 5.8 and 6.4 depending on limestone reactivity but not on limestone excess quantities. The buffer effect ensures a constant SO_2 removal rate even with extreme fluctuations in the intake concentration of the sulfur dioxide in the flue gas.

This process is very effective in removing HCl, HF, and SO_2 and heavy metals present in the flue gas. Typical wet scrubber performance is shown in Table 2. High utilization of the limestone accompanied with high removal efficiency of acid gas constituents in this process is achieved due to the process operating at its optimum pH range for absorption (higher pH in the upper loop is favorable for absorption) and the reagent dissolution (lower pH in the lower loop is favorable for limestone dissolution).

The Noell wet scrubbing process is preferable for the following reasons:

a) more stringent future legislation to reduce emission limits can easily be met; and
b) the better by-product quality allows the use of the end product in the gypsum industry.

Table 3 shows the required FGD-gypsum quality standards. To meet this standard in some cases, additional gas cleaning devices must be installed upstream of the scrubber for removal of toxic compounds, such as heavy metals or aromatic hydrocarbons.

Table 2 Removal Efficiencies by Noell Wet Scrubbing Process

Item	Units	Raw Gas	Clean Gas	Removal eff. (%)
SO_2	mg/Nm^3 (dry)	1296	16.9	98.7
HCl	mg/Nm^3 (dry)	117.4	0.9	99.2
HF	mg/Nm^3 (dry)	9.7	0.2	97.9
DUST	mg/Nm^3 (dry)	5.7	<1	>82.0

Table 3 Gypsum Specification (Germany)

Moisture	F	(%)	<10
Purity	R°	(%)	>95
pH	pH		5–8
Whiteness		(%)	80
Odor	Neutral		
Particle Size (<32 μm)		(%)	>60
Impurities (max. ≤5.20%)		(%)	<5
Magnesium Oxide	MgO Water Soluble	(%)	<0.10
Sodium Oxide	Na_2O Water Soluble	(%)	<0.06
Chloride	Cl^- Water Soluble	ppm	<100
Calcium Sulfite	$CaSO_3 \cdot 1/2\ H_2O$	(%)	<0.50
Organic Matter		(%)	<0.1
Aluminum Oxide	Al_2O_3	(%)	<0.3
Iron-III-Oxide	Fe_2O_3	(%)	<0.15
Silica (HCl-insoluble)	SiO_2	(%)	<2.5
Calcium and Magnesium Carbonate	$CaCO_3 + MaCO_3$	(%)	<1.5
Potassium Oxide	K_2O Water Soluble	(%)	<0.06
Ammonia and Nitrate	$NH_3 + NO_3^-$	(%)	0

Advantages of the wet limestone scrubbing process include:

a) excellent buffering for the fluctuating SO_2 load in the flue gas (especially for flue gas from an incinerator);
b) reduced danger of scaling;
c) the lowest absorbent cost combined with excellent stoichiometry; and
d) easy process control and adjustment.

However, this process application is also limited due to the generation of waste water.

NOELL COMBINED PROCESS

In order to achieve the highest noxious gases removal efficiencies but also to avoid waste water treatment, Noell developed the combination process. This process combines the advantages of spray absorption and the wet scrubbing process to form a unique system.

Figure 6 shows one possible arrangement of the combination process where separate fly ash from reaction by-product may be required. A dust collect is placed between downstream of the waste boiler and upstream of the spray absorber. If the fly ash can be disposed with the reaction products from flue gas cleaning, dust collection at this point is not necessary. Furthermore, in order to minimize the formation of dioxins, it is essential to quench the flue gas as quickly as possible in the spray dryer.

After passing through the dust collector, the flue gas enters the spray dryer absorber with a downstream high-efficiency dust collector. In this stage, the flue gas is conditioned, prescrubbed, and rapidly quenched to minimize Dioxines/Furans formation. The scrubbing slurry for this stage is the discharge from the subsequent wet scrubbing stage. Noxious substances in the flue gas react with the remaining unused absorbent in the slurry droplets. Fine dust is agglomerated and bonded to the surface of the wet particles during the drying process. Heavy metals can be removed either by injection of activated carbon between spray dryer and dust collector (normally using a fabric filter) or by adding chemicals to the wet scrubber discharge to form an organosulphide to avoid re-evaporation of heavy metals during the drying process.

The portion of the reaction products are collected in the bottom of the spray absorber and withdrawn as fine-grained free-flowing by-product. The fine dust present in the flue gas,

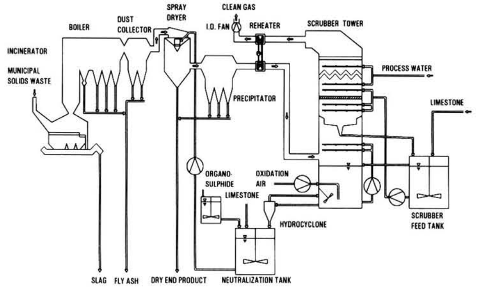


FIGURE 6. Noell combined process (spray dryer followed by Noell wet scrubber).

Table 4 Combined Noell Process Used in MSW Incineration

Installation	Flue Gas Flow Rate Nm^3/hr, wet	Year of Commissioning
GKS Schweinfurt, Germany	3×41000	1993
HKW München Nord, Germany	2×143000	1994
MVA Fürth, Germany	2×34000	1996
AVA Nijmegen, Netherlands	1×75000 1×143000	1995

after the spray dryer absorber, is collected in the downstream dust collector prior to entering the wet scrubber. Since the heavy metals are present in these fine dust particles, their removal in this dust collector minimizes interfering reactions by heavy metals in the wet scrubber. In addition, the further reaction between acid gases and unused sorbent in the particles can take place on the filter cake as mentioned before, further enhancing total noxious gases removal efficiency.

Pre-scrubbed flue gas leaves the spray absorber system and enters a heat exchanger if required. In the heat exchanger, heat is removed from the inlet flue gas of the wet scrubber and is used to reheat the flue gas from the wet scrubber.

The last stage of flue gas cleaning is via the Noell double-loop limestone scrubber.

CONCLUSIONS

Spray dryer absorber (SDA), double-loop wet scrubber (WS), and the combination of SDA and WS are being used on full-scale waste incinerators to meet emission standards and permit conditions. The selection of which flue gas cleaning process to use depend on:

a) Emission limits required;
b) Process by-product disposal requirements;
c) Whether waste water can be tolerated and discharged cost effectively; and
d) Site space requirements.

Table 5 Emission Limits for Waste Incinerator (with 11% O_2)

Item	TA Luft 74 (mg/m^3)	TA Luft 86 (mg/m^3)	17. BlmSchV (mg/m^3)
Dust	100	30	10
Carbon Monoxide	100	100	50
Org. Matter (as total C)	50	20	10
Sulphur Oxides (SO_2)	—	100	50
Nitrogen Oxides (NO_2)	—	500	200
Chlorine Compound (HCl)	100	50	10
Fluorine Compound (HF)	5	2	1
Dioxines, Furanes (TE)	—	—	0.1×10^{-6}

Quite different gas cleaning processes might be necessary depending on these criteria. For example, the spray absorption process may be a suitable choice, if it is possible for: the residual high pH by-product to be deposited in a licensed waste disposal area, discharge of waste water is not permitted, and only moderate levels of SO_2 removal are required. If on the other hand, waste water disposal is not an issue and a very high removal efficiency with the lowest consumption of absorbent and a usable by-product is required, the Noell wet scrubbing process may be more appropriate. Finally, if waste water discharge requirements are stringent, high acid gases removal as well as heavy metals and dioxines removal are required, and high pH solids disposal is problematic the Noell combined process is the most advantageous solution. Table 4 lists commercial installations for Noell combined process. Guaranteed emission limits for these facilities will comply with the strict standard of the 17th BImSchV standard shown in the Table 5. The start-up of the first Noell combination process on a full commercial scale will take place in Schweinfurt, Germany at the end of 1993.

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