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### AMERICAN INSTITUTE of CHEMICAL ENGINEERS

# **ENVIRONMENTAL PROGRESS**

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

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Cover: Micro-Switch, a Honeywell Division, of Free-port, Illinois, was recently awarded a first-place trophy by the IEPA for "Outstanding Illinois Industrial Pollu-tion Control Program of the Year." Micro-Switch has a record of continuous improvement in waste-water treatment. Photo courtesy of Micro-Switch

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### Editorial

## Assessing and Managing Environmental Risk

**Raymond C. Loehr** 

H. M. Alharthy Centennial Chair and Professor, Environmental and Water Resources Engineering Program, The University of Texas at Austin, and Chairman, Science Advisory Board, U.S. Environmental Protection Agency

Over the past decades, many laws been enacted, regulations promulgated, and policies imple-

mented to control environmental problems. These efforts have led to national benefits such as fewer fish kills, less air pollutants emitted, and hazardous wastes being better controlled. However, the landscape of environmental problems facing us in the future looks different than the one we have seen in the past. The stubborn portions of older environmental problems and newly identified problems will be increasingly difficult to solve. Conventional "command and control" regulatory approaches do not appear sufficient to deal with the remaining and emerging problems.

Assessment of these problems, identifying the relative health and environmental risks associated with them, as well as finding reasonable approaches to reduce these risks are a continuing major challenge. A recently issued report by the EPA Science Advisory Board<sup>1</sup> (SAB) offers suggestions about how this challenge can be met. Key among the eight findings and ten recommendations is the concept of relative environmental risk.

Environmental contamination can adversely affect human health, ecological health and the quality of life, i.e., pose an environmental risk. If the relative risk of environmental problems can be assessed, the magnitude and impact of such problems can be better understood. This allows different problems to be compared in common terms. It also allows risk reduction options to be evaluated from a common basis. The ability to systematically compare different environmental risks can help determine which problems are most serious and require the most urgent attention. This ability becomes increasingly valuable as the number and seriousness of environmental risk can be used to establish priorities based on the greatest opportunities to reduce risk, total risk to human health and the environment will be reduced in a more efficient way.

The SAB report includes ideas about how to identify and compare environmental risks and about options that can be considered to control environmental problems and reduce environmental risks. It is, however, but one step on a long road toward a better understanding of environmental risks. The SAB report should stimulate much discussion about what are the major environmental problems and how should they be controlled, discussion in which engineers should have a strong and active role.

<sup>&</sup>lt;sup>1</sup>Science Advisory Board, "Reducing Risk: Setting Priorities and Strategies for Environmental Protection," U.S. Environmental Protection Agency, SAB-EC-90-021, Washington, D.C. 1990.

**Environmental Shorts** 

## Advanced Environmental Laws & Regulations Course

New Oil Pollution Act of 1990, 75 new regulations, new state laws and regulations, new enforcement trends . . .a lot is happening in the environmental field! How can businesses keep up with all these developments and avoid company problems, avoid fines and even avoid criminal prosecution?

To help companies stay abreast of the ever-changing regulatory developments and prepare for the major new developments, Government Institutes, Inc. is offering its acclaimed Advanced Environmental Laws & Regulations Course on June 27-28, 1991, in Breckenridge, Colorado and an August 19-20 in Hilton Head, South Carolina.

This intensive yet comprehensive two-day course is led by environmental professionals who work daily in the environmental field. By analyzing the impacts of the new developments, these speakers are prepared to succinctly describe what the complex laws and regulations mean in practical terms.

Topics to be covered include: the Clean Air Act; Clean Water Act; RCRA Reauthorization and Corrective Action; Developments in Identification, Listing & Delisting of Hazardous Waste; TCLP; Land Ban Restrictions; OSHA Developments; SARA/Superfund; TSCA and Enforcement Activities.

For more information or to register for the Advanced Environmental Laws & Regulations Course please contact Colleen Sullivan at Government Institutes, Inc., 966 Hungerford Drive, #24, Rockville, MD 20850; 301/251-9250; FAX 301/251-0638.

### Erratum conceled istors

In "Integrated Model for Predicting the Fate of Organics in Wastewater Treatment Plants" by Govind, Lei and Dobbs [*Environmental Progress* **10**, 13–23 (1991)] the footnote at the bottom of page 23 should read: "A commercial PC version of the FATE model is available from Morris Computer Systems Inc., 10270 Wayne Avenue, Cincinnati, OH 45215. Telephone: 1-800-MCS-9630. A demo version is available upon request."

### Just Released Proceedings Help Businesses Identify New Opportunities in The Environmental Market

To help businesses identify these market opportunities, the proceedings from Government Institutes' 1991 "Environmental Markets" conferences, entitled Industrial & Federal Environmental Markets Report, has just been released. With the new information gained from these proceedings, businesses will be better able to assess these growth opportunities and develop a winning market strategy.

In the Industrial & Federal Environmental Markets Report, 16 national experts who practice daily in the environmental industry provide these insights in sections on: Air Pollution Markets; Hazardous Waste Markets: CERCLA/Superfund Site Cleanups; Hazardous Waste Markets; RCRA Hazardous Management and Disposal; Solid Waste Markets; Underground Storage Tank Markets: Environmental Audits and Real Estate Assessment Markets; Factors Affecting the Asbestos Marketplace; Environmental Law: the Driving Force Behind the Federal Environmental Market; Environmental Law and the Federal Environmental Contractor; Federal Procurement Process; Department of Energy Environmental Markets; Department of the Navy Priorities; The Army Installation Restoration Program and the Formerly Used Defense Site Program; Air Force Environmental Programs; and Industrial Environmental Markets.

According to G. David Williams, Vice-President of Government Institutes, Inc., publisher of the In-'dustrial & Federal Environmental Markets Report, "The industrial environmental market alone is valued at over \$100 billion and growing annually."

The 320-page three-ring binder, Industrial & Federal Environmental Markets Report is available for \$189 U.S./\$191 outside U.S. (price includes shipping and handling charges) from Government Institutes, Inc., 966 Hungerford Drive, #24, Rockville, MD 20850; (301) 251-9250. ocean of air

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It's a matter of life and breath."



## **Washington Environmental Newsletter**

### **CLEAN WATER ACT REAUTHORIZATION**

### **Key Senators To Introduce Sweeping Legislation**

Manditory toxics reduction programs for non-industrial toxics and expanded citizen enforcement authority are among a broad group of proposals being weighed by Senate environment committee staffers preparing legislation to reauthorize the Clean Water Act (CWA). However the most controversial issue facing Congress during the debates, namely the wetlands issue, is notably absent from proposals put forth thus far.

The comprehensive bill, sponsored by the Senate Environment & Public Works Committees ranking Republican John Chafee (R-RI) and Environmental Protection Subcommittee Chair, Max Raucus (D-MT), was slated for introduction on April 11. A series of hearings is planned for the period between April 23 and May 21, 1991.

General topics to be addressed in the new bill have been outlined and each topic listed will be addressed in amendments, or a series of proposals that in total will add-up to a very broad bill.

Some amendments and proposals being discussed are:

• To require sewage treatment plants to limit discharges of waste oil, household toxics and other pollutants into the waste stream.

• One proposal suggests amending the Act to allow citizens to sue for past violations, overriding a recent Supreme Court decision that ruled that citizens may sue for current violations only, and not past infringements.

• There will be recommended changes that would allow for enforcement against discharges which exceed applicable water quality standards, while noting that current standards are not enforceable.

• There are proposals for "toxic reduction action programs" that target non-industrial toxic pollutants being discharged into sewage plants. The draft proposes that would require publicly owned treatment works serving populations over 50,000 to develop and implement reduction programs, subject to EPA review.

• Pollution prevention is also stressed in the "pretreatment" and "effluent guidelines" draft proposals. For instance, process changes and materials substitution could be used in establishing categorical standards for specific sectors of industry that discharge into sewage systems. Because such standards reflect end-of-pipe technology that may cause air and land pollution, one proposal would require EPA to prohibit discharges to air or land as part of a compliance strategy to prevent water pollution.

• Other amendments and proposals are equally complex and will be monitored and reported on as debate proceeds to shake-out issues. As it stands now, the bill will be an inclusive attempt to address all issues affecting clean water, including the clean water role of the U.S. Geological Survey, the Fish and Wildlife Service and other federal agencies.

Meanwhile, Sen. Dave Durenberger (R-MN) told a Council of Infrastructure Financing Authorities that he will propose his own bill on the issue, separate from a committee clean water bill.

We expect that the CWA will go thru as many iterations, compromises and debates, as did the Clean Air Act, and no final action will take place until after the next elections.

Stay tuned—Washington issues, like the Washington weather, change when least expected...

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

### **Book Review**

Control of Fugitive and Hazardous Dusts Pollution Technology Review No. 192, C. Cowherd, P. Englehart, G. E. Muleski, J. S. Kinsey, and K. D. Rosbury, Noyes Data Corporation, Park Ridge, NJ (1990) 230 pages [ISBN No.: 0-8155-1253-8] U.S. List Price: \$64.00

Control of Fugitive and Hazardous Dusts is a compilation of information published in two earlier documents by these authors.

The book consists of two parts. After a brief review of the relevant sections of the existing regulations, the sections of the first part focus on specific source categories such as paved and unpaved roads, open waste piles and staging areas, dry surface impoundments, landfills, land treatment, and waste stabilization. The sections are well-written with an overview of the source category, and description of emission characteristics and mechanisms. Available emission factors are presented to enable the analysis of the operative nature of control options. Regulatory formats are provided to enable the reader to see how the compliance action addresses the requirements. Detailed appendices provide information on the terminology used, a generic costing methods, modeling techniques for health risk information and generic methods of sampling and analysis of materials from hazardous material treatment, storage, and disposal facilities.

The introduction to the second part of the book identifies emission control mechanisms. The three following chapters describe the three major mechanisms of contaminated soil reentrainment in the air through vehicles, soil movement and wind erosion, and include available dust control options. The final chapter addresses the relevant principles of dust control plan formulations. The

#### AIChE 1991 Publications Catalog

For a complete listing of all process control titles available from AIChE consult our 1991 Publications Catalog. If you have not received your copy, please send your request to: AIChE Publications Sales Department, 345 East 47th St., New York, N.Y. 10017. section includes appendices on equipment decontamination and worker protection and the non-air impacts of dust suppressant measures.

A timely publication, this book provides a concise manual describing the necessary design and implementation steps required to achieve compliance with RCRA requirements for the control of fugitive and hazardous dusts.

John B. Rajan, P. E. Chemical Technology Division Argonne National Laboratory 9700 South Cass Avenue Argonne, IL 60439

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### **Video Review**

The Audit: What You Must Know to Perform, Manage or Survive an Audit, Stone & Webster Management Consultants, Inc., New York, NY, \$800

This review is a first for both the author and *Environmental Progress* — but it's clearly a logical development as new methods of information transfer such as videotaped training programs appear. It's great to be able to focus our first review on a first-rate video-tape and an excellent example of the new era of technical communications.

Stone and Webster, in my opinion, has produced an excellent training film for people who conduct audits and those who receive audits dealing with the following topics:

- Safety audit
- Environmental audit
- Corporate performance review
- Quality management examinations

The presenters are not actors but are actually members of Stone and Webster's staff. Each of the three speakers, however, comes across as well as a professional TV performer. I was impressed by their easy, conversational style.

The tape has several different (each approximately 10-14 minutes long) segments dealing with:

- Introduction to the audit
- Basic audit concepts
- Interviewing skills
- Logic diagrams
- Audit control and data tracking
- The audit report; structure and audience
- Writing reports; words and style

The goals of the tape are clearly specified at its beginning when the lecturer notes what you will (should) learn:

What an audit is and how to use it

- How to plan and monitor an audit
- How to interview and solicit information and to get the facts
   How to organize information

In the introduction, the lecturer uses the space shuttle explosion as an example to discuss the importance of a management audit by comparing or contrasting it to a technical audit. The goal of management is to help ensure that a company has a commitment to safety and the environment. He points out that an audit is costly and should therefore be designed and implemented to provide good recommendations that would benefit and be of value to the company. The audit, he stresses, should be balanced: it should cite both the good and bad-strengths as wells as the weaknesses-of the program evaluated.

The second module on the videotape deals with Basic Management Concepts:

- Audit
- Audit parts
- Wish list

Modules 3, 4, and 5 deal with interview techniques, the logic diagram and audit control. I found the section on interviewing-or how to conduct an interview to get the interviewee to talk and supply information-useful and most interesting. Various barriers-breaking techniques are detailed and the interview planning logic is discussed. Also intriguing, was the tape's discussion of the logic diagram in which one progresses from the facts to findings and conclusions or recommendations. The logic diagram is a major controlling element which guides the audit from the inception of the project through the conduct of the audit and the development or scrutiny of the report itself. This tape segment concluded with recommendations based on the foregoing steps.

The final two sections of the tape discuss the basic principles of report

writing. Since this is my area (I teach our department's required course entitled "Communications for Chemical Engineers"), I listened intently to the advice given. The lecture was good and full of excellent advice on standard writing procedures that I teach in my course (and found in numerous books on technical writing) such as:

- Use audience analysis
- Use the active rather than passive tense
- Write, sort, rewrite
- Write long, condense later
- Let the draft "cool" before editing
- Be diplomatic

This is the first videotape I have reviewed, so I have little basis for comparison. On the other hand, there is ample reason to be complimentary. This is a good effort both technically (in content) and procedurally (in production). The material gives sound advice. The speakers are excellent and have a good, clear, interesting speaking style that holds your attention. And clearly, the topic is one of current importance.

I would suggest, however, that a hard copy of the graphics, tables, charts, etc., would be useful. I kept stopping the tape to make notes of the many excellent ideas it presented. Perhaps, Stone and Webster could produce a short manual embodying the key advice in print.

The audit is an excellent tape. When I finished listening to it, I was left wanting even more—more examples—perhaps even an example interview. I throughly enjoyed the videotape and believe the time watching it was well spent.

Gary F. Bennett, editor Department of Chemical and Biomechanical Engineering The University of Toledo Toledo, OH 43606.

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## Software to Study Environmental Effects of Hazardous Waste Sites

Ashok Kumar

University of Toledo, Toledo, OH

and

### Jae B. Lee

### U.S. Environmental Protection Agency, Chicago, IL

As a result of the Resources Conservation and Recovery Act (RCRA), the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), and the Clean Air Act, computer models are being used in the planning and decision making process of hazardous waste sites. Typical activities include remedial investigation, corrective action, remedial action, operation and maintenance, enforcement and assessment for these sites. The computer models are used to assess air dispersion, ground water flow, surface water transport, estimating ground water rontamination levels, designing liners, landfills, incinerators, estimating risk and exposures and estimating remedial cost.

The development of software for hazardous waste sites has focused on different media, pathways and processes. The available software may be grouped into the following categories:

(i) Air Dispersion Models: These models are used for predicting the transport of pollutants (gases and particulates) emitted from different remediation efforts, assessing volatilization of pollutants from hazardous waste sites and landfills, and determining evacuation areas in emergency situations (e.g., sudden release of hazardous materials). The most popular models are those available from the bulletin board operated by the United States Environmental Protection Agency (EPA). Complete details are given in a paper by Kumar and Mohan [1]. Models developed by private companies and research organizations are also useful [2]. The EPA has certain preferred models for air regulatory work based on criteria such as shortterm (2-24 hours) vs. long-term (monthly, seasonal or annual), type of terrain (simple or complex), type of source (single, multiple, buoyant or complicated) and land use (urban or rural). Before conducting the work, one should check with a regional EPA office for current regulatory requirements related to modeling. In a survey it was found that the Industrial Source Complex Model (ISC) is the widely used model in the EPA regional offices for superfund sites [3 & 4].

(ii) Ground Water Models: The models are widely used for hazardous waste sites. They are capable of locating areas of potential environmental risk, identifying pollution sources, evaluating design alternatives and assessing possible remedial plans. During the last three decades several hundred models have been developed and evaluated in industry, universities and regulatory agencies. These models can be used to determine the nature and extent of contamination during the remedial investigation, and to evaluate the effectiveness of various remedial alternatives during the feasibility study [5]. In 1978, The International Ground Water Modeling Center (ICWIC) was established by The Lucleowh Leasense Leasense

(IGWMC) was established by The Holcomb Research Institute at Butler University in Indianapolis, Indiana. IGWMC acts as a clearing house for gound water models. A list of models used by the EPA regional offices is given in Table I. The models are available from IGWMC.

(iii) Surface Water Models: These models cover different processes which occur in rivers, streams, lakes, reservoirs, estuaries and bays. Modeling of estuaries and bays is the most complex because of the nature of forces acting on the waters. The surface water models used for hazardous materials may include processes taking place in the water and in the sediments. A list of 21 models is given in Table 2 which have been used for the assessment of hazardous waste sites at the EPA offices [3]. They represent a variety of water body categories, temporal scales, type of contamination sources and dimensions. The models can be used for impact analysis, examination of remedial actions and illegal dumping or accidental discharges. Some regulatory guidelines do exist for the development, evaluation and application of surface water models for hazardous waste sites.

The views expressed in this paper are those of the authors.

- (iv) Hazardous Waste Engineering Models: This class of models is used in the design and evaluation of treatment, storage and disposal facilities, hazardous waste incinerators, soil liners, dikes and different remedial techniques. Four models which have been used by the EPA for hazardous waste sites are listed in Table 3 [3]. The models are not available from the National Technical Information Service (NTIS).
- (v) Exposure/Risk Assessment Models: The models are related to transport and fate modeling for air, water and land systems. They are capable of performing screening analysis and detailed analyses and include interactive graphics. Current efforts in the field is towards integrating models for different media to develop integrated packages. A list of models used for superfund sites is given in Table 4 [3]. The Center for Exposure Assessment Modeling at the EPA

#### Table 1 Examples of Ground Water Models

SATURATED FLOW: AGU-1, AQSIM, AQUIFEM, AQUIFEM-1, AQUIFER, AQUIFLOW, BASICGWF, BIDAT-HS2, BURGEAP-2, BURGEAP-3, CONS2-1D, CONSOL-1, CONSP9LINLO-2D, CRREL, DELPET, DELTA, DELTIS, DEWATER, DFT/C1D, DISIFLAG, ECPL704-F3, RO-011, ECPL723-G2-L2440, FE3DGW, FEMSAT, FESOSPF, FEWA, FIELD-2D, FLOP, FREESURF-1, FRONT, GM5, GROMAGE, GROMULA, GWEFLOW, GWMD-3, GWPATH, GWSIM, GWUSER, IASIFMAM, IDPNGM, INVERS, ISOQUAD, KRGW, LAFTID, LAS, MAQWF, MODFLOW, NLRGFM, NMFD-3D, PE, PEP, PLASM, PLIN, PUMPTEST, QUDMA, RADFLOW, ROCMAS-HW, SEEP(VM)-3D, SEEP2(VM)-2D, SGMP, SICK-100, ST-2D, STFLO, STRESEEP-2D, SYLENS, TER2AGI, TETRA, TGUESS, THCVFIT, THWELLS, TIMLAG, TOFEM-N, TRIGAT-HSI, TSSLEAK, USGS-2D-FLOW, USGS-3D-FLOW, VARQ, VDM, VTT, VTTSS-2, VTTSS-3

SOLUTE TRANSPORT: AGU-10, ASCOT, BEAVERSOFT, BIO-1D, CADIL, CATTI, CFITIN, CHEMRANK, COLUMN2, CXTFIT, DISPEQ, DOSTOMAN, DSTRAM, FEMA, FEMTRAN, FEMWASTE, FLAMINCO, FRONTTRACK, GEOFLOW, GETOUT, GGCP, GROWKWA, GS2, GS3, GWSIM-2, IONMIG, ISL-50, ISOQUAD-2, GASOLINE, MAQWQ, NITROSIM, NMODEL, ONE-D, PATHS, PISTON, PLUME-2D, PORFLOW II, RANDOM WALK, RESTOR, RITZ, SATRA-CHEM, SATURN-2, SBIR, SESOIL, SOLUTE, SOTRAN, SWIFR, TRANQL, TRIPM, USGS-2D-TRANSPORT/MOC, VAM-2D, VAM-3D, WALTON-35, WASTE

MULTIPHASE FLOW: ASSP, BURGEAP-1, CCASM, CHARGR, GEOTHER, INTERFACE, MOTGRO, MULKOM, MUSHRM, SEAWTR, SWANFLOW, SWIFT, SWIGS-2D, SWIN, SWSOR

**FRACTURED ROCK:** BACRACK, CHAINT, CRACK, FEM301, FRACFLOW, FRACPORT, FRACSL, FRACSOL, FRACT, FRACTEST, MOTIF, NETFLOW, ROCMAS-H, ROCMAS-HM, ROCMAS-HS, ROCMAS-THM, STAFAN-2, STAFF-2D, SUGARWAT, TOUGH, TRACR-3D, TRAFRAP-WT, TRUCHN/ZONE, TRUMP

#### ESTIMATE POSITION OF WATER TABLE: DRAINMOD

HYDROCHEMICAL: BALANCE, EQ3NR/6, EQUILIB, GEOCHEM, MINEQL2, PHREEQE, PROTOCOL, REDEQL-UMD, REDEQL.EPA, SOLMNEQ, SOLMNQ, WATEQ-2, WATEQ-3, WATEQF

HEAT TRANSPORT: CFEST, EP21-GWTHERM, FLOTRA, GAFETTA, GREASE-2, HOTWTR, HST3D, MAGNUM-2D, MARIAH, MATTUM, MMT-1D, MMT-DPRW, PORFLOW, PORFREEZE, PT, PT-CCC, SANGRE, SCHAFF, SEFTRAN, SHAFT-79, SHALT, SPLASHWATR, SUTRA, SWENT, SWIFT, TEXASHEAT, TRANS, UWIS-2D-TRANSPORT, VADOSE

VARIABLY SATURATED FLOW: FEATSMF, FEMWATER, FLO, FLOWVEC, FLUMP, GRWATER, HSSWDS, INFGR, INFIL, LANDFIL, MUST, ONE STEP, SEEPV, SOIL, SOILMOP, SOMOF, SWATRE, TRUST, UNSAT-1, UNSAT-1D, UNSAT-2, UNSAT-H, VS-2D, WATERFLO

CALCULATION OF HEADS FOR DEWATERING: GW1

M8 May, 1991

	Table 2 Examples of Surface Water Models					
Computer Model	Organization	Purpose				
ACTMO	U.S. Dept. of Agriculture, Agricultural Research Service	nonpoint source model applicable to agricultural areas				
AGRUN	Water Resources Engineers, Inc.	nonpoint source model applicable to agricultural watersheds				
ARM-2	U.S. EPA, ERL-Athens, GA	estimate pollutant loadings in agri- cultural areas				
CAFE	Dept. of Civil Engineering, MIT Cambridge, MA	two dimensional hydrodynamics sim- ulation in estuaries				
CHNHYD	Environmental Sciences Division, Oak Ridge National Laboratory, TN	simulating flows and water surface el- evation in river networks				
CHNTRN	Environmental Systems Division, Oak Ridge National Laboratory, TN					
CREAMS	U.S. Dept. of Agriculture, Science and Education Admin.	estimate pollutant loadings from ag- ricultural areas				
СТАР	HydroQual, Inc.	concentration distributions in water column & sediments				
DWOPER	Hydrologic Research Laboratory Na- tional Weather Service, NOAA	simulating river flow				
FETRA	Battelle, Pacific Northwest Laboratories	transport of contaminants, sedi- ments, in well-mixed estuaries				
HEC-2	U.S. Army Corps of Engineers, Davis, CA	water surface profile in rivers for a steady flow discharge				
HEC-6	U.S. Army Corps of Engineers, Davis, CA	profile water surface and stream bed				
MEXAMS	Battelle Pacific NW Lab	fate and transport of metals in aquatic systems				
MICHRIV	U.S. EPA, ERL-Duluth	transport in water and sediment in streams and nontidal rivers				
NTS	U.S. EPA, ERL-Athens, GA	estimate nonpoint source pollutant loads in urban and rural areas				
SEDONE	Oak Ridge National Laboratory, TN	simulating hydrodynamic flow and sediment transport				
SERATRA	Battelle, Pacific Northwest Laboratory for U.S. EPA	transport of contaminants and sedi- ments in rivers				
SLSA	HydroQual, Inc.	concentration distribution in water and sediments of rivers and lakes				
TDMECS	Rand Corporation, Santa Monica, CA	flow and contaminant transport in es- tuaries and coastal seas				
WATFLOW	Rand Corporation, Santa Monica, CA	hydrodynamic flow in rivers and es- tuaries				
WQSM	Rand Corporation, Santa Monica, CA	flow and transport in well-mixed es- tuaries and coastal seas				

supports the models given in this table and can be down-loaded from their electronic bulletin board.

The review of models given in this paper is not a comprehensive one. There are many more models which are available in literature. However, the list of models given in this paper can be used as a starting point for selecting an appropriate model for your professional needs.

Some suggestions for future improvements in the availability and the use of the software to study environmental effects of hazardous waste sites are: (i) availability of software through NTIS and through a bulletin board system similar to air quality models,

- (ii) guidelines for evaluation of models, and
- (iii) development of a list of acceptable screening models and a list of models for detailed/refined analysis.

Availability of personal computers has had a significant impact on the development of models to study environmental effects of hazardous waste sites. New models are constantly being developed and the old models are being updated. It is hoped that you will find a model (or models) which meet your needs.

	Table 3 Examples of Hazardous Waste	Engineering Models
Computer Model	Organization	Purpose
EMBM	U.S. EPA (RREL, Cincinnati, OH)	simulation of industrial incineration
GARDS	U.S. EPA (HWERL, Cincinnati, OH)	evaluate earth dike structures at hazardous waste facilities
HELP	U.S. EPA (HWERL, Cincinnati, OH)	simulation of hydrologic effects at hazardous waste sites
SOILINER	U.S. EPA (HWERL, Cincinnati, OH)	simulation of liquid infiltration through compacted soil liner

In the meantime regulatory guidelines will become clearer for hazardous waste sites.

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Table 4 Examples of Exposure/Risk Assessment Models				
Computer Model	Organization	Purpose		
DYNHYD-4	Federal Water Quality Administration U.S. Dept. of Interior	flow, transport and degradation in rivers and estuaries		
DYNTOX	Limno-Tech	predict concentrations of contaminants in surface waters		
EXAMS-2	U.S. EPA (ERL-Athens, GA)	predict concentrations of contaminants in surface waters		
GEMS	U.S. EPA (ERL-Athens, GA)	air, soil and ground-water analysis		
HSPF	U.S. EPA (ERL-Athens, GA)	predict contaminant concentrations in surface and ground water		
MINTEQ-2	U.S. EPA (ERL-Athens, GA)	predict contaminant concentrations in surface and ground		
PRZM	U.S. EPA (ERL-Athens, GA)	predict contaminant concentrations in ground water		
SARAH-2	U.S. EPA (ERL-Athens, GA)	predict contaminant concentrations in ground water		
SHAPE	U.S. EPA (ORD)	population exposure to carbon monoxide		
SWMM-4	U.S. EPA (ERL-Cincinnati, OH)	non-point source runoff from urban area		
WASP-4	U.S. EPA (ERL-Athens, GA)	predict contaminant concentrations in surface waters		
WQA	U.S. EPA (ERL-Athens, GA)	predict contaminant concentrations in runoff, surface and ground waters		

## The Formation of Inorganic Particles During Suspension Heating of Simulated Wastes

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Measurements of metal partitioning between the fine condensation aerosol and the larger particles produced during rapid heating of aqueous and organic solutions containing metal additives with widely varying volatilities were made in a laboratory-scale furnace operated over a range of temperatures (900 to 1500 K). A stream of monodisperse droplets (nominal diameter of 36  $\mu$ m) was injected into an isothermal, laminar drop-tube reactor, quickly developing into a stream of droplets with heterogeneous size distribution due to droplet collision and coalescence. Aqueous solutions containing nitrates of cadmium, lead and nickel gave rise to particles with trimodal size distributions. Partitioning of the larger particles between a residual mode (particle aerodynamic diameter,  $D_{p,aero} > 7 \mu m$ ) and an intermediate mode  $(1 \ \mu m > D_{p,aero} > 7 \ \mu m)$  is suggestive of particle porosity variation. In addition, ultrafine particles, with submicron aerodynamic diameter, were formed, both by the anticipated vaporization pathway and by an unexpected explosive fragmentation mechanism. The higher volatility of the chloride than the oxide was evidenced by an enhanced inorganic aerosol formation during the high temperature treatment of a nickel chloride solution. The oxidative burning of organometallic solutions of nickel and lead produced only particles of submicron aerodynamic size.

#### INTRODUCTION

Currently global natural fluxes of some metals, such as cadmium, are exceeded by anthropogenic fluxes [1]. The emission of metal aerosols from incinerators represents a potential contribution to the anthropogenic sources. Recent studies by the United States Environmental Protection Agency (EPA) and by European investigators have included measurements of metal emissions [1-5]. Not only are the ultrafine particles produced during thermal decomposition difficult to capture by electrostatic precipitation [ $\delta$ ], these particles penetrate the deep lung when inhaled [7]. A second reason for the study of the fine inorganic particles generated by incinerators is that they provide a signature that can be used for source attribution. The amount and composition of ambient inorganic particulate matter varies widely with geographical location and time as a consequence of the wide variability of source emissions [ $\delta$ ]. Therefore, a mechanistic understanding of the physical and chemical processes governing inorganic particle formation during waste incineration is needed both for the development of

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FIGURE 1. Hypothesized pathways of inorganic particle formation.

better control technologies to reduce the contribution of inorganic aerosols to atmospheric pollution and for the development of better source allocation models that utilize ambient metal particulate markers.

Studies of the chemical and physical transformations of mineral matter in coal combustion have provided considerable insight into the formation of inorganic aerosols. It has been shown that coal fly-ash is bimodally distributed with respect to size [9-13]. The larger residual ash particles, with diameters in the range of 1 to 50  $\mu$ m, contain trace amounts of volatile species concentrated at the particle surface. The submicron particles, on the other hand, are enriched with the more volatile coal mineral matter constituents [10]. Laboratory studies [11-13] have shown that these particles are produced by the nucleation and subsequent coalescence and coagulation of a portion of the vaporized fly-ash. Although the mass fraction of submicron particles is typically much less than that of the residual particles, the submicron particles are much more numerous and contain most of the particle surface area available for heterogeneous condensation of inorganic vapor; hence, volatile species enrichment is observed in the submicron particles.

While the subsequent processes of nucleation, condensation, coalescence and coagulation govern the composition and size distribution within the submicron size mode, vaporization is largely responsible for the quantity of inorganic aerosol generated. Barton et al. have developed a metals-partitioning model based on equilibrium volatilization [14]. Vaporization of inorganic species is complicated by simultaneous chemical processes such as decomposition, chlorination, oxidation and



FIGURE 2. Drop-tube reactor assembly. The furnace is equipped with a Berglund-Llu device for monodisperse droplet generation, optical access for microphotography, and a cascade impactor for particle size classification.

reduction. For example, the vaporization of refractory oxides has been found to involve the more volatile suboxide or metal species as well as the oxide itself [15,16]. Comparisons of vaporization calculations with experimental and field measurements indicate that the equilibrium assumption is not always reasonable [17].

To gain a better understanding of the mechanisms for metal partitioning between the fine condensation aerosol and the larger particles produced by the residue of metal-containing liquid wastes burned in suspension, a laboratory study was conducted. Effects of waste composition, waste atomization, local gas composition and furnace temperature were studied. This paper presents data that are used to evaluate the hypothesis that submicron particles are formed primarily by a vaporization mechanism, as indicated in Figure 1.

#### EXPERIMENTAL

#### **Apparatus and Methods**

A laminar flow drop-tube furnace was used to vaporize aqueous and organic droplets containing cadmium, lead and nickel additives. The general features of the laboratory-scale facility are shown in Figure 2. A stream of monodisperse droplets is injected down the centerline of the reaction zone contained by an electrically heated quartz tube (47 mm I.D.). The isothermal reaction zone length is 33 cm, representing a nominal bulk gas residence time of 1.4 s. Mixtures of oxygen and nitrogen, separately metered and totalling 6.0 standard liters/ min, are preheated to the furnace wall temperature prior to entry into the reaction zone. In these experiments furnace wall temperatures ranging from 900 to 1500 K were maintained.

Streams of monodisperse droplets are generated by a Berglund-Liu type device [18] located at the entrance to the isothermal reaction zone. Droplet size, droplet velocity and interdroplet spacing are controlled (though not independently) by choice of orifice size, vibrator frequency and liquid supply pressure [19]. Satellite droplets are virtually eliminated by operating the Berglund-Liu device at an optimum frequency. Nominally, the test liquid is supplied at a pressure of 3.7 atm to a 20 µm diameter orifice which is vibrated at 215 kHz, producing a uniform stream of 36  $\mu$ m diameter droplets with an interdroplet spacing of 2.7 diameters and a velocity of 21 m/s. However, due to the rapid deceleration of the droplets falling in a linear array, droplet collisions and coalescence ensue. To minimize these droplet interactions, dispersion gas is introduced coaxially with the droplets, resulting in a dilute spray being developed approximately 3 cm into the reaction zone. The droplet size distribution is measured in situ by microphotography.

The entire product stream is recovered and rapidly quenched with an inert dilution gas. Particle deposition in the collection



FIGURE 3. Vapor pressure curves.



FIGURE 4. Droplet size distributions. Measurements at 0.5, 1, 2 and 3 cm into the reaction zone were taken. The lognormal probability distribution functions are calculated to fit measurements of between 50 and 100 droplet diameters.

probe is avoided by transpiring more dilution gas radially through the probe's inner wall. The particles and gases are then passed through an Andersen Mark II cascade impactor for on-line aerodynamic size classification of particles between 0.4 and 15  $\mu$ m (see Figure 2). Impaction stages are greased to minimize particle bounce. The particles with aerodynamic diameter less than 0.4  $\mu$ m pass through the impactor and are collected on an absolute final filter (0.2  $\mu$ m pore diameter).

Each solution studied contained one metal additive. The use of single metal solutes obviates the need for detailed chemical analysis of the collected particles; i.e., gravimetric analysis provides the particle aerodynamic size distribution directly. Inversion and smoothing of the data are performed using the algorithm of Markowski [20].

#### **Metals Studied**

Cadmium, lead and nickel compounds were chosen for study because: (1) these metals are of highest priority in EPA's proposed regulations [21], and (2) these metals incorporate a wide range of volatilities (Figure 3). Cadmium is a refractory oxide, with a sublimation point of 1832 K for the oxide and a boiling point of 1038 K for the pure metal. Lead oxide boils at 1745 K, whereas lead metal boils at 2013 K. Nickel oxide and nickel metal both have boiling points of about 3000 K. Nitrates of cadmium  $\{Cd(NO_3)_2 \cdot 4H_2O\}$ , lead  $\{Pb(NO_3)_2\}$  and nickel {Ni(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$ } were dissolved into distilled water in a mass concentration of 1.5 percent. In the high temperature environment of the drop-tube furnace, after the water has boiled away, the nitrate decomposes by releasing nitrogen dioxide and oxygen and the thermodynamically stable oxide species, the monoxide, is formed. The particle then is heated to the temperature of the surrounding gas, vaporizing at a rate dependent on its vapor pressure history and total residence time.

Nickelous chloride {NiCl<sub>2</sub>·6H<sub>2</sub>O} was dissolved into distilled water and injected into the furnace under the same conditions as were the nitrates. The vapor pressure of nickel chloride being much higher than that of nickel oxide, submicron particle formation is expected to be enhanced when nickel chloride is present. Organic solutions of lead and nickel were also fired. Cyclopentadienyl nickel {Ni(C<sub>3</sub>H<sub>3</sub>)<sub>2</sub>}, or nickelocene, was dissolved in toluene, and lead octoate {Pb(C<sub>7</sub>H<sub>15</sub>COO)<sub>2</sub>} was dissolved in a mixture of 20 percent mineral oil and 80 percent heptane. The solutions were injected under both oxidizing and inert conditions. Submicron particle formation is expected to be enhanced in flames since particle temperatures are elevated due to the exothermicity of hydrocarbon combustion. Particle temperatures were not measured in this study.

#### **RESULTS AND DISCUSSION**

Before presenting the particle size distribution data resulting from the suspension heating of the solutions just described, droplet size distribution data collected for the droplets during a transition period of droplet collision (in the initial 10 percent of the reaction zone) are presented.

#### **Droplet Collision and Coalescence**

The data displayed in Figure 4 show a change from an initially monodisperse droplet stream to a polydisperse condition over a very short distance and during a very short time period. With dispersion gas, droplets cease growing after travelling 3 cm into the reactor (after approximately 2 ms). By this point the droplet distribution has become bimodal, with approximately 25 percent of the droplets retaining their original size. The other 75 percent of the droplets grow in size to produce a heterogeneous distribution with a mean diameter 1.7 times the initial diameter. This represents the coalescence of about five droplets of original size. The fraction of droplets with diameters greater than 100  $\mu$ m is approximately 1.5 percent. Thus, the introduction of dispersion gas coaxially with the droplet stream limits the extent of droplet collision and coalescence, but does not eliminate these interactions.

The occurrence of droplet collision and coalescence in these experiments is important in that it determines the subsequent formation of a particle size distribution without fragmentation and vaporization (i.e., assuming one particle per droplet). It is also important in that it results in the formation of oversize droplets that can pass through the reaction zone before the solvent has completely evaporated. In the case of an aqueous solution, droplets with diameters exceeding 100  $\mu$ m exit the formation of oversize droplets, all particle size distribution manimize the formation of oversize droplets, all particle size distribution measurements were made for tests with dispersion gas on.

The ability of predicting droplet growth in this essentially one-dimensional system poses a challenging problem. An initial collision of two identical droplets appears to be very sensitive to small fluctuations in the parameters associated with droplet generation and gas introduction. Calculations based on steady processes fail to predict the observed behavior. Once an initial collision takes place, the instability of the stream of polydisperse droplets results in a rapid succession of collisions. Although this process appears to be inherently chaotic, the overall result is reproducible and can be well-defined statistically. More sensitive measurements of system nonuniformities and nonlinearities are needed before attempting to model droplet growth by collision and coalescence.

#### **Heating of Metal Nitrate Solutions**

Figure 5a shows particle aerodynamic size distributions for the heating of aqueous solutions containing nitrates of nickel, cadmium and lead. The curves represent results from the deconvolution of the masses measured on each of the eight cascade impactor stages and on the final filter. From Figure 5a it is seen that data deconvolution does not alter qualitatively the trend of the original data. However, the shape of the calculated distribution near the upper and lower diameter endpoints is arbitrary. The data exhibit a trimodal character. The aerodynamic diameters (referenced to spherical geometry and unit density) marking mode boundaries are: less than 1  $\mu$ m (submicron mode); between 1 and 7  $\mu$ m (intermediate mode); and greater than 7  $\mu$ m (residual mode). The occurrence of three modes is surprising. Submicron particles from vaporized metal oxide and residual particles from condensed phase passage through the furnace were expected.



FIGURE 5. Aerodynamic particle size data for tests with nickel, cadmium and lead nitrate solutions. The distribution graphs (left) include the actual cascade impactor stage data in histogram form and a regression fit to the output of the data inversion code [20]. The submicron mode mass fraction graph (top right) includes vapor pressure curves (dashed) for CdO and PbO.

The unexpected occurrence of an intermediate particle size mode is likely due to a varying particle porosity created during decomposition and heating. Droplet size distribution heterogeneity results in particles ranging in initial size by a factor of three (Figure 4). In addition, the larger droplets require longer times to evaporate, leaving little or no time available for exposure of the particles to the hot reactor gases. Thus, variations in particle porosity arise due to variations in the incipient particle size and subsequent particle residence time. The net effect of increased porosity on aerodynamic size classification is a decrease in aerodynamic diameter.

The integrated mass percents of metal oxide collected in each of the three modes of the aerodynamic size distribution are shown as functions of furnace temperature in Figure 5b for the nickel, cadmium and lead nitrate solutions studied. Also shown are the equilibrium vaporized mass percents (based on furnace volumetric flow rate) of CdO and PbO. Equilibrium vaporization of NiO is insignificant at temperatures below 2000 K.

Nickel oxide submicron particle fractions of between 35 and 40 mass percent were measured over the temperature range studied. It is unlikely that these submicron particles could have formed via a vaporization route due to the extremely low volatility of nickel and its oxides. In addition, the almost total lack of dependence of submicron particle fraction on temperature implies that vapor pressure is not the driving force of submicron particle formation. An alternative pathway for submicron particle formation is that of explosive fragmentation. More direct evidence of this mechanism is presented elsewhere [22].



FIGURE 6. Submicron particle mass fraction measurements for tests with the nickel nitrate and nickel chloride solutions.

#### Vaporization of Nickel Chloride

Suspension heating of aqueous droplets containing nickel chloride produced higher fractions of submicron particles than similar heating of aqueous droplets containing nickel nitrate (Figure 6). Further, unlike the nickel nitrate results, the nickel chloride data exhibit a temperature dependence more indicative of a vaporization mechanism. This is the expected result since the vapor pressure of nickel chloride is much higher than that of nickel oxide. In general, the vaporization of metals will be enhanced by the pressure of chlorine.

#### **Burning of Organometallic Compounds**

At a furnace wall temperatures ranging from 900 K, suspension burning of nickelocene dissolved in toluene produced solely submicron particles (Figure 7), in quantitative agreement with the amount of metal input. When heated in an inert environment (nitrogen), and otherwise under identical conditions, only residual particles, with aerodynamic diameter greater than 7  $\mu$ m, were produced. The absence of submicron particles in the pyrolysis experiments, conducted at 900 K, suggests that the nickelocene, which has a sublimation temperature of about 405 K, decomposes prior to any appreciable vaporization of the nickel. Clearly, oxidation has a dominating influence on the size distribution of inorganic particles. A major effect is likely to be enhanced vaporization due to both increased particle temperature and increased particle residence time (since droplet burning rates are much greater than droplet





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FIGURE 8. Observed pathways of inorganic particle formation.

vaporization rates). Explosive fragmentation during decomposition may also be enhanced by combustion.

At furnace wall temperatures ranging from 900 to 1500 K, suspension heating of lead octoate dissolved in mineral oil and heptane produced entirely submicron particles in both oxidizing and reducing environments. The formation of particles entirely of submicron size during pyrolysis at 900 K may be explained by either of the following hypotheses. First, vaporization of the lead octoate may occur prior to its decomposition to the less volatile lead or lead oxide. We were unable to find vapor pressure data on lead octoate with which to support or reject this conjecture. However, in nickelocene pyrolysis at 900 K, as already stated, thermal decomposition is apparently too rapid to allow for appreciable metal vaporization. Second, the use of a two-component solvent (mineral oil and heptane) with different component boiling points allows for the possibility of secondary atomization of the droplets. This explosive phenomenon would produce a shower of droplet fragments that would then yield submicron particles directly. Further work is needed to confirm or dismiss this possibility.

#### SUMMARY

From the results reported here, it is hypothesized that inorganic particle formation occurs by both vaporization and explosive fragmentation, as depicted in Figure 8. This is a more complicated picture than originally proposed (Figure 1). Monodisperse droplets become polydisperse by colliding and coalescing, resulting in oversize droplets that can pass through the reaction zone. Evaporation of the solvent follows, with the possibility of secondary atomization producing submicron particles if multicomponent solvents are used. The residual particles decompose to form particles of varying porosity, as well as submicron particle vaporization, with subsequent nucleation and condensation upon quenching, also results in the formation of an inorganic aerosol.

These findings indicate that a closer examination of the role of fragmentation in inorganic particle formation is needed to elucidate its mechanism. Analysis of sampled particles by scanning electron microscopy in a subset of these experiments provides more direct evidence of the physical transformations hypothesized in this paper. This work is presented separately [22].

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## MIN-CYANIDE: An Expert System for Cyanide Waste Minimization In Electroplating Plants

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Rapid development of technologies and production systems is often accompanied by the increased generation of hazardous or toxic wastes. Among these wastes, waste solutions containing cyanide cause a particularly serious problem, threatening both public health and environment. It appears that the best way to minimize the cyanide-containing wastes is to reduce their production in electroplating plants. Numerous techniques have been developed for this purpose, and much experience has been gained by applying such techniques. An expert system, MIN-CYANIDE, has been constructed to assist engineers and technicians in the source reduction of cyanide-waste solutions in an electroplating plant by resorting to these techniques and experience, and to train plant operators in the application of the techniques. MIN-CYANIDE evaluates options, such as dragout minimization, bath-life extension, rinse-water reduction, replacement with a non-cyanide solution, use of an alternative plating technique, and improvement of the operating procedure; furthermore, it identifies the most effective among them. The knowledge about the cyanide source reduction is acquired from available publications, represented by numerous fuzzy or non-fuzzy heuristic rules, and codified into a commercial export system shell, Personal Consultant Plus, on an IBM PC/AT compatible computer. MIN-CYANIDE provides a userfriendly interface; in operating it, the user answers various questions concerning the operational situations of the production and/or current equipment and techniques in the plant. In response, MIN-CYANIDE will present instantaneously a series of options for cyanide minimization and eventually rank them.

#### INTRODUCTION

Release of any hazardous and toxic waste is detrimental to environment and public health. Obviously, the minimization of hazardous or toxic waste is an urgent social concern. Waste minimization can be realized through source reduction, recycling, and treatment, among which source reduction is preferred from an environmental perspective. Source reduction is an activity that reduces or eliminates the generation of hazardous waste at the source, usually within a process [I].

Among the variety of wastes generated in the metal finishing industry, cyanide-containing waste solution of electroplating plants is of particular concern because of its high toxicity. Although some operating rules are adopted in many electroplating plants to reduce the generation of cyanide-containing waste solution, the prevailing practice resorts mainly to the treatment of the solution. This will lead to substantial expenditure for the treatment of the waste solution and disposal of the resulting sludge [2].

Effective reduction of cyanide release and in the cost for

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FIGURE 1. Typical electroplating process

treating the waste can be facilitated by a computer system, which performs like a domain expert. This computer system should be able to make intelligent decisions concerning strategies for minimizing cyanide waste. Nevertheless, it is extremely difficult, if not impossible, to formulate such strategies purely mathematically and algorithmically; in other words, we can not resort to a traditional technique to develop a computer system necessary for performing mainly symbolic rather than numeric operations. Fortunately, Artificial Intelligence (AI) techniques enable us to do so.

AI is concerned with mimicking human intelligence on a computer, primarily with non-numeric processes that frequently can be complex, uncertain, and ambiguous. An expert system is an information system that can pose and answer questions relating to information borrowed from human experts and stored in the system's knowledge base [3]. Such a system can offer intelligent advice about a processing function. Our intention is to develop an expert system for generating guidelines for minimizing quantitatively and toxically cyanide waste in effluents from an electroplating plant.

#### **PROCESS DESCRIPTION**

A typical electroplating process is depicted in Figure 1. In the process, each workpiece is cleaned to remove dirt and oil prior to plating/stripping. This involves electrocleaning, alkaline cleaning, acid cleaning, and rinsing. Some of the unit operations in the process, such as electrocleaning and rinsing in the first two tanks, are optional. Furthermore, the unit operations of stripping and rinsing in the fifth and sixth tanks, respectively, are not required for the parts whose metal plate layers do not have to be removed. After plating/stripping, each part should be cleansed twice; finally, it is air-dried.

The generation of waste streams within the typical plating operation is also illustrated in Figure 1. Among the major waste streams, those containing cyanide are spent plating/ stripping solution, rinse water, spills, leaks, drippings, and off-specification products. Other major waste streams include spent alkaline solution, alkaline rinse water, spent acidic solution, acidic rinse water, and plating tank filter waste.

### CYANIDE WASTE MINIMIZATION STRATEGIES

Reducing the generation is the most effective means of minimizing cyanide waste. This can be realized by decreasing dragout, extending bath life, lessening rinse water, substituting cyanide solutions, altering plating metals and/or techniques, and implementing sound operating practices [2,4]. These strategies are elaborated below.

Decreasing drag-out is mainly achieved by appropriately positioning a workpiece on a plating rack, lowering the concentration of plating bath constituents, reducing the speed of a workpiece withdrawal from solution to allow sufficient drainage time, increasing the temperature of plating solution, lowering the surface tension of a solution, and improving the dragout recovery.

Extending bath life is accomplished by reducing the dragin through improved rinsing, deionizing or distilling make-up water, regenerating plating/stripping solution through impurity removal, applying mechanical agitation instead of air sparging, rationally designing and maintaining rack, increasing the



FIGURE 2. Example of rule firing in a hierarchically connected rule set

purity of anodes, properly removing the anode, and returning solution to the manufacturer.

Lessening rinse water is implemented by installing automatic flow controls, agitating the rinse bath, using multiple rinse tanks and spray and fog nozzles, resorting to closed-loop rinsing, reusing rinse water, and judiciously arranging barrel rinsing.

Some non-cyanide solutions have been identified as substitutes [2]. These include pyrophosphate copper plating solution, non-cyanide cadmium plating baths, and non-cyanide silver stripping solutions. In addition, alternative plating metals and/ or techniques such as cadmium ion and aluminum vapor depositions have been proposed.

Finally, the following operating practices are recommended: waste stream segregation, operator training and closer supervision, spill and leak prevention, preventive and corrective maintenance, management initiatives, and material/waste tracking and inventory control. The detailed description for each strategy can be found in a recent report [2].

#### EXPERT SYSTEM DEVELOPMENT

The development of an expert system comprises three major steps [5]. The first is knowledge acquisition to identify the knowledge or expertise appropriate for the program construction and understanding. The knowledge is generally classified as the so-called *shallow knowledge* which relies on the experience of human experts, and the so-called *deep knowledge* which uncovers the fundamental cause-effect or causal relationship. The second is knowledge representation. Any knowledge captured is to be explicitly encoded in some effective representation schemes. The third is knowledge manipulation on a computer. In this step, a manipulation scheme must be selected, and a computer system based on AI techniques is constructed to manipulate the knowledge for reaching the goals.

An expert system, designated as MIN-CYANIDE, has been successfully built. The knowledge base of the system contains all the detailed cyanide minimization strategies; its database contains the process data and constraints; and its inference engine contains a forward chaining mechanism for the rea-



FIGURE 3. Structure of knowledge base

soning based on the information input and the knowledge installed in the system. Since the construction of a knowledge base is of utmost importance, the representation and manipulation schemes of the acquired knowledge should be delineated.

#### **Knowledge Representation**

The selection of knowledge representation schemes is carried out based on the feature of domain knowledge. The selected schemes should be conducive to the reduction of loss of knowledge and to the enhancement of efficiency of knowledge manipulation.

While some of the information available from operators of an electroplating plant is imprecise or very imprecise, some is not. For instance, no instruments exist generally to measure the surface tension and viscosity of a solution in a bath. The information about them can only be roughly provided by the operators based on their experience and subjective judgement. Furthermore, most of the individual strategies for the cyanide waste minimization are expressed as causal or cause-effect relationships. Consequently, both fuzzy and crisp (non-fuzzy) rules can be used for the knowledge representation. In contrast to the crisp rules, the fuzzy rules contain ambiguous linguistic terms, such as HIGH, FAST, and MODERATE. These terms should be treated according to fuzzy set theory [6]. The basic concepts of fuzzy set theory can be found in APPENDIX A. The following example illustrates the representation of a fuzzy rule by fuzzy logic:

- IF the surface tension of a solution is HIGH, AND
- the operating temperature of a bath is not HIGH,
- THEN it is definite that there is MUCH drag-out.

It is extremely difficult to identify a sharp boundary between the concepts of low and high surface tension, low and high temperatures, and much and less drag-out. This is circumvented by resorting to fuzzy set theory. Fuzzy sets A, B, and C are defined for the concepts of high surface tension, high operating temperature, and much drag-out, respectively. The rule is thus represented by the following fuzzy logic relation.

$$A \wedge \overline{B} \rightarrow C$$
 (1)

There are 114 rules embedded in the knowledge base. As illustrated in the hypothetical example in Figure 2, Rule 11 is activated if its antecedent is satisfied most completely compared with the antecedents of the remaining rules including Rule 12, Rule 13,  $\cdots$ , Rule 1M. Then, a rule, e.g., Rule 21, among Rule 21, Rule 22,  $\cdots$ , Rule 2N, at the next level, is fired, whose antecedent is most precisely mapped to the consequent of Rule 11. This process is repeated until a goal is reached. All the rules are distributed in a hierarchically structured knowledge base; see Figure 3. Strategy control, a main frame in the first layer, processes the information input by the user to identify an appropriate strategy, a subframe in the second layer, for reasoning about the problem. Each subframe in the second layer consisting of a set of detailed strategies.

#### **Knowledge Manipulation**

A decision is to be made according to the rule firing. In the evaluation of rules encoded in a knowledge base, the MAX-MIN algorithm is employed at each rule level. For instance, to make an intermediate decision at the *j*-th rule level, N rules are evaluated in accordance with the algorithm, i.e.,

$$\mu_{j}(x) = \max_{j \in J} \{ \min_{i \in I} \{ \mu_{i1}(x), \mu_{i2}(x), \dots, \mu_{ik}(x), \dots, \mu_{iN}(x) \} \}$$
(2)



FIGURE 4. Quantitative representation of fuzzy linguistic terms, low, moderate, and high temperature's

where

- $\mu_{ik}(x) =$ membership function of variable x in fuzzy set k representing the k-th antecedent of the i-th rule at the j-th level
- $\mu_j(x)$  = membership function of variable x in the fuzzy set pertaining to the rule selected to be fired at the jth level
- x = variable

Figure 4 gives an example of the definition of membership functions related to the fuzzy linguistic terms, LOW, MOD-ERATE, and HIGH TEMPERATURE's. The membership function of variable *T* in fuzzy set *E* corresponding to HIGH TEMPERATURE,  $\mu_{EH}(T)$ , is defined as

$$\mu_{EH}(T) = \begin{cases} 0, & T \le 200^{\circ} \mathrm{K} \\ \frac{T - 200}{200}, & 200^{\circ} \mathrm{K} < T \le 400^{\circ} \mathrm{K} \\ 1, & T > 400^{\circ} \mathrm{K} \end{cases}$$
(3)

The mathematical forms of the membership functions,  $\mu_{EL}(T)$ , and  $\mu_{EM}(T)$ , for the linguistic terms, LOW and MODERATE TEMPERATURE's, respectively, can be derived from the same figure.

The algorithm is described in detail through the following example. The antecedent of the rule in the preceding subsection can be represented by the truth value expression

$$\tau_i = \min\{\mu_A(x), \ \mu_{\overline{B}}(x)\} \tag{4}$$

where

$$\tau_i$$
 = truth value of rule *i*  
 $\mu_A(x)$  = membership function of variable *x* in fuzzy set  
 $A$   
 $\mu_{\overline{x}}(x)$  = membership function of variable *x* in the

 $d_{\overline{B}}(x) =$  membership function of variable x in the complement of fuzzy set B

Operation MIN yields a set of M truth values through evaluation of the membership functions of all the related rules. Then, a single rule is selected by performing operation MAX, i.e.,

#### **MIN-CYANIDE ADVISOR**



FIGURE 5. Example of a man-machine communication with an input of fuzzy information

$$\tau = \max\{\tau_1, \tau_2, \cdots, \tau_M\}$$
(5)

This selected rule is activated or fired. The same operation is repeated at the succeeding level based on the information received from the preceding level (see APPENDIX B).

Note that a crisp, or non-fuzzy, rule is a special case of fuzzy rules. An example of a crisp rule is as follows:

IF the plating type is HEAVY\_COPPER\_PLATING, THEN pyrophosphate copper plating solution can be substituted for cyanide solution.

The concept of HEAVY\_COPPER\_PLATING can be described as a crisp set, H, which is a special case of a fuzzy set. Thus, the membership function of plating type in set H,  $\mu_{H}$ , is equal to 1 when the plating type is HEAVY\_COPPER\_PLAT-ING; otherwise, it is 0. Note that no conflict can occur even when both fuzzy and crisp rules reside in the same knowledge base.

#### IMPLEMENTATION

The present expert system is constructed on a personal computer, IBM PC/AT compatible. The knowledge base occupies approximately 60,000 bytes of memory. A commercial expert system shell, Personal Consultation Plus [7] serves as the software. Even the user who is not sufficiently familiar with the expert system can view knowledge about the cyanide minimization on the system or modify the existing one to enhance it.

MIN-CYANIDE is a system of the question-conclusion type. The system poses a set of questions; the number and type of them depend on the information input. The user is required to respond to the questions. The response must naturally be consistent with the user's knowledge; however, it could be imprecise. The user is then immediately provided with the conclusions.

Figure 5 illustrates a snapshot of a screen exhibiting the question, "How high is the viscosity of the solution?": Eight dots among ten are highlighted using an arrow key by the user: it indicates that the user has 80% confidence in the statement that the viscosity of the solution is high. Figure 6 gives a complete example of running the system for the drag-out minimization. The summary of the questions posed by the system and the data input by the user are shown in the upper part of plating performed?", are of the yes/no type, and others, e.g., "What is the roughness of surface of a workpiece?" are of the ambiguous type. The lower part of the figure demonstrates the conclusions and recommendations resulting from the fuzzy and non-fuzzy information provided by the user.

This case gives rise to the conclusion of EXCESS.CYANIDE, thereby indicating that an excessive cyanide-containing waste solution is generated due to drag-out. This, in turn, prompts four recommendations for reducing drag-out. These recommendations are associated with different certainty factors which are the measures of confidence. While the levels of confidence of the first two are 100% (omitted from the screen), those of the remaining two are 80% and 63%. These levels of confidence of the recommendations are evaluated by the system based on the fuzzy information input. The user can either accept or reject these recommendations based on the subjective judgement in the light of actual conditions in the plant.

MIN-CYANIDE was repeatedly test-run. Without fail, it has yielded with dispatch a multitude of conclusions with regard to the generation of cyanide waste and the recommendations for its minimization. These conclusions and recommendations appear to be valid and practical judging from the currently available knowledge and information [2,4].

#### CONCLUSIONS

An expert system, MIN-CYANIDE, has been successfully developed for the minimization of cyanide waste in an electroplating plant. This expert system resorts to the fuzzy logic for knowledge representation and manipulation of imprecise information. Thus, it can operate on the ambiguous linguistic terms frequently adopted by experts.

MIN-CYANIDE has a highly user-friendly interface which enables the user to communicate easily with the system. The system can instantaneously draw a conclusion about the current status of the generation of cyanide waste. If the generation is excessive, the system can immediately propose a multitude of recommendations to alleviate the situation.

In developing the present system, we have had minimum participation by domain experts. Naturally, the system can be enhanced substantially by continually extracting additional knowledge from domain experts and incorporating it into the system.

#### ACKNOWLEDGMENT

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## APPENDIX A: BASIC CONCEPTS OF FUZZY SET THEORY

Zadeh [8] writes: "The notion of a fuzzy set provides a convenient point of departure for the construction of a conceptual framework which parallels in many respects the framework used in the case of ordinary sets, but is more general than the latter and, potentially, may prove to have a much wider scope of applicability, particularly in the fields of pattern classification and information process. Essentially, such a framework provides a natural way of dealing with problems in which the source of imprecision is the absence of sharply defined criteria of class membership rather than the presence of random variables."

This appendix outlines the basic concepts of fuzzy set theory. Some simple examples are provided for clarification [6].

Type of plating performed	BARREL_PLATING
High viscosity of a solution	80%
Roundness of surface of a workpiece	70%
High concentration of thebath	20%
High surface tension of the solution	60%
Workpiece shape	ROUND
Angle of inclination of the workpiece to horizontal in degree	45
Difficulty to dry the workpiece	NO
Draining time (sec)	12
Rinsing type	FLOW
CONCLUSIONS AND SUGGESTIONS	
CURRENT STATUS OF CYANIDE WASTE GENERATION	
EXCESS_CYANIDE	
SUGGESTIONS TO DRAG OUT MINIMIZATION	
(1) Barrel plating causes excess drag out. You may need to tr	y rack plating.
(2) There is excess rinse water. You may need to install a de	ad rinsing system.
(3) Please increase the bath temperature (80%)	

(4) Please smoothen the workpiece (63%)

#### FIGURE 6. Example of a solution for drag-out minimization SUMMARY OF THE DATA INPUT TO MIN-CYANIDE ADVISOR

**Definition 1.** Assume that we have a set of N discrete decision alternatives

$$X = (x_1, x_2, \cdots, x_N)$$
 (A-1)

Fuzzy set U of X is characterized by the membership function,  $\mu_U(x_i)$ , which associates with every member of X a number in the interval [0,1], representing the degree to which element  $x_i$  belongs to set U; it can be written as

$$U = \left\{ \frac{\mu_U(x_1)}{x_1}, \frac{\mu_U(x_2)}{x_2}, \cdots, \frac{\mu_U(x_N)}{x_N} \right\}$$
(A-2)

U is a set of N tuples. The actual value of  $\mu_U(x_i)$  needs to be assigned subjectively by a decision maker.

**Example 1.** Let  $X = \{0, 30, 60, 90, 120, 150, 180, 210, 240\}$  represent a set of temperatures (\*K) of the solution in a tank. Let U represent the set called "moderate" temperature. Then, depending upon the temperature, every member of X is assigned a membership, leading to, e.g.,

$$U = \left\{ \frac{0}{0}, \frac{0.25}{30}, \frac{0.50}{60}, \frac{0.75}{90}, \frac{1.0}{120}, \frac{0.75}{150}, \frac{0.50}{180}, \frac{0.25}{210}, \frac{0}{240} \right\}$$
(A-3)

Its simple interpretation is as follows: If the temperature of the solution in the tank is  $120^{\circ}$ K, it is indeed a "moderate" temperature; however, the temperature of  $90^{\circ}$ K can also be regarded as belonging to set U, with a lesser degree, namely, 0.75, and so on.

**Definition 2.** Let U and V be two fuzzy sets over X. The intersection operation, denoted by  $U \cap V$ , is also a fuzzy set over X. The membership function of  $C = U \cap V$  is obtained as

$$\mu_C(x_i) = \mu_U(x_i) \wedge \mu_V(x_i) \tag{A-4}$$

for all  $x_i \in X$ . Notice that " $\wedge$ " represents the minimum operation. In addition, this operation corresponds to logical "and" connective.

Example 2. Let

$$U = \left\{ \frac{0}{0}, \frac{0.25}{30}, \frac{0.50}{60}, \frac{0.75}{90}, \frac{1.0}{120}, \frac{0.75}{150}, \frac{0.50}{180}, \frac{0.25}{210}, \frac{0}{240} \right\}$$
(A-5)

and

$$V = \left\{ \frac{1.0}{0}, \frac{0.75}{30}, \frac{0.50}{60}, \frac{0.25}{90}, \frac{0}{120}, \frac{0}{150}, \frac{0}{180}, \frac{0}{210}, \frac{0}{240} \right\}$$
(A-6)

Then, the intersection of sets U and V would be

$$C = U \wedge V = \left\{ \frac{0 \wedge 1.0}{0}, \frac{0.25 \wedge 0.75}{30}, \frac{0.50 \wedge 0.50}{60}, \frac{0.75 \wedge 0.25}{90}, \frac{1.0 \wedge 0}{120}, \frac{0.75 \wedge 0}{150}, \frac{0.50 \wedge 0}{180}, \frac{0.25 \wedge 0}{210}, \frac{0 \wedge 0}{240} \right\}$$
$$= \left\{ \frac{0}{0}, \frac{0.25}{30}, \frac{0.50}{60}, \frac{0.25}{90}, \frac{0}{120}, \frac{0}{150}, \frac{0}{180}, \frac{0}{210}, \frac{0}{240} \right\}$$
(A-7)

**Definition 3.** Let U and V be two fuzzy sets over X. The union operation denoted by  $U \cup V$  is also a fuzzy set over X. The membership function of  $D = U \cup V$  is

$$\mu_D(x_i) = \mu_U(x_i) \lor \mu_V(x_i) \tag{A-8}$$

for all  $x_i \in X$ . Notice that " $\lor$ " represents the maximum operation. Furthermore, this operation corresponds to logical "or" connective.

**Example 3.** The union of the same fuzzy sets, U and V, as those in Example 2, gives

$$D = U \vee V = \left\{ \frac{0 \vee 1.0}{0}, \frac{0.25 \vee 0.75}{30}, \frac{0.50 \vee 0.50}{60}, \frac{0.75 \vee 0.25}{90}, \frac{1.0 \vee 0}{120}, \frac{0.75 \vee 0}{150}, \frac{0.50 \vee 0}{180}, \frac{0.25 \vee 0}{210}, \frac{0 \vee 0}{240} \right\}$$
$$= \left\{ \frac{1.0}{0}, \frac{0.75}{30}, \frac{0.50}{60}, \frac{0.75}{90}, \frac{1.0}{120}, \frac{0.75}{150}, \frac{0.50}{180}, \frac{0.25}{210}, \frac{0}{240} \right\}$$
(A-9)

**Definition 4.** The complement of fuzzy set U defined over domain X is also a fuzzy set denoted by  $\overline{U}$ . The membership function of  $\overline{U}$  is obtained as

$$\mu_{\overline{U}}(x_i) = 1 - \mu_U(x_i) \tag{A-10}$$

for all  $x_i \in X$ .

**Example 4.** Let  $X = \{0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3\}$  represent the viscosities of a solution (Pa.s). Let U represent the set called "desirable" viscosity. Assume that each viscosity is assigned a membership, leading to, e.g.,

$$U = \left\{ \frac{0}{0.4}, \frac{0.2}{0.6}, \frac{0.4}{0.8}, \frac{0.6}{1.0}, \frac{0.8}{1.2}, \frac{1.0}{1.4} \right\}$$
(A-11)

Then,

$$\overline{U} = \left\{ \frac{1.0 - 0}{0.4}, \frac{1.0 - 0.2}{0.6}, \frac{1.0 - 0.4}{0.8}, \frac{1.0 - 0.6}{1.2}, \frac{1.0 - 1.0}{1.4} \right\}$$
$$= \left\{ \frac{1.0}{0.4}, \frac{0.8}{0.6}, \frac{0.6}{0.8}, \frac{0.4}{1.0}, \frac{0.2}{1.2}, \frac{0}{1.4} \right\}$$
(A-12)

 $\overline{U}$  can be interpreted as the set of "not desirable" viscosity.

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#### APPENDIX B: RULE ACTIVATION BY MAX-MIN OPERATION

A decision is to be made by evaluating all the related rules at different levels in a knowledge base. The evaluations are carried out according to the MAX-MIN algorithm, i.e.,

$$\mu_{j}(x) = \max_{\substack{j \in J \\ i \in I}} \{ \min_{i \in I} \{ \mu_{i1}(x_{1}), \mu_{i2}(x_{2}), \\ \cdots, \mu_{ik}(x_{k}), \cdots, \mu_{iN}(x_{N}) \} \}$$
(B-1)

where

- $\mu_{ik}(x)$  = membership function of variable x in fuzzy set k representing the k-th antecendent of the i-th rule at the j-th level
- $\mu_j(x)$  = membership function of variable x in the fuzzy set pertaining to the rule selected to be fired at the j-th level

 $x, x_k = \text{variables}$ 

The MAX-MIN algorithm is implemented in two stages. The antecedent of a rule can be represented by a truth value expression.

$$\tau_i = \min\{\mu_{i1}(x_1), \mu_{i2}(x_2), \cdots, \mu_{ik}(x_k), \cdots, \mu_{iN}(x_N)\}$$
(B-2)

The MIN operation yields a set of truth values through evaluation of the membership functions of all the rules. Then, a single rule is selected by performing the MAX operation, i.e.,

$$\tau = \max\{\tau_1, \tau_2, \cdots, \tau_M\}$$
(B-3)

This selected rule is activated or fired. The same operation is repeated at the succeeding level based on the information received from the preceding level.

**Example.** Assume that a set of rules at the *j*-th level is as follows:

Rule 1. If  $\underline{A}$  and  $\underline{B}$ , then  $D_1$ Rule 2. If  $\overline{\underline{A}}$  and C and E, then  $D_2$ Rule 3. If  $\overline{\underline{B}}$  and E, then  $D_3$ 

where A, B, C, and E represent different fuzzy sets which are related to certain linguistic terms;  $\overline{B}$  is the complement of fuzzy set B; and D<sub>1</sub>, D<sub>2</sub>, and D<sub>3</sub> represent different decisions. Also assume that the membership functions,  $\mu_A(x_1)$ ,  $\mu_B(x_2)$ ,  $\mu_C(x_3)$ , and  $\mu_E(x_4)$ , have values of 0.3, 0.4, 0.8, and 0.7, respectively.

The task is to select a decision among  $D_1$ ,  $D_2$ , and  $D_3$  at the *j*-th level. In other words, one rule among the three should be activated based on the fuzzy information. This is accomplished by the MAX-MIN operation in two stages.

First, the MIN operation on the antecedent of each rule need be carried out. This gives rise to the following three truth values.

$$\tau_{1} = \min\{\mu_{A}(x_{1}), \mu_{B}(x_{2})\}$$

$$= 0.3 \land 0.4$$

$$= 0.3 \qquad (B-4)$$

$$\tau_{2} = \min\{\mu_{\overline{A}}(x_{1}), \mu_{C}(x_{3}), \mu_{\overline{E}}(x_{4})\}$$

$$= 0.7 \land 0.8 \land 0.7$$

$$= 0.7 \qquad (B-5)$$

 $\tau_3 = \min \{ \mu_{\overline{B}}(x_2), \mu_{E}(x_4) \}$ 

Second, the MAX operation is performed on these three truth values as follows:

$$\tau = \max\{\tau_1, \tau_2, \tau_3\}$$
  
= 0.3 \vdot 0.7 \vdot 0.6  
= 0.7 (B-7)

This value of 0.7 corresponds to Rule 2 which should be activated; in other words, decision  $D_2$  should be made. This decision becomes one of the antecedents of some rules at the (j+1)-th level. The same MAX-MIN operation is carried out at the (j+1)-th level, (j+2)-th level,  $\cdots$ , and so on, until a final decision is reached.

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## Field Verification of Predictive Modeling of Organic Compound Removal by Biological Wastewater Treatment Processes

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This paper presents the results of a field study conducted to examine the accuracy achieved when modeling the removal of organic compounds by biological wastewater treatment processes. Special emphasis is placed on determining the specific removal pathway, accuracy for three compounds, believed to the removed primarily by only one pathway. Off-gas chloroform measurements made through use of a surface isolation flux chamber were modeled to within two percent, as were measurements reflecting the biodegradative removal of methanol. Varying degrees of accuracy were obtained for the chlorophenolic compounds examined.

#### **INTRODUCTION**

Concern over the intermedia transfer of potentially toxic compounds from the aqueous phase to the atmosphere and sludges during wastewater treatment has led to the development of several mathematical models designed to predict the fate of organic compounds during treatment. An issue only recently being addressed is quantification of the accuracy of these models, including removal pathway specific accuracy.

A computer model of organic compound removal by biological treatment processes receiving pulp and paper industry wastewaters has previously been developed by the National Council for Air & Stream Improvement (NCASI) [1], the industry's environmental research organization. The model simulates compound removal by four different pathways; forced stripping, natural volatilization, biosorption and biodegradation.

James J. McKeown is deceased.

Evaluation of the NCASI organic compound removal model (NOCEPM) accuracy is addressed in this paper based on field measurements made at an activated sludge process treating pulp and paper industry wastewaters. The study involved completion of three tasks; (a) establishment of the historical organic compound loading rates and overall removal efficiencies of the host site activated sludge process, (b) measurement of the off-gas concentration of volatile compounds over the aeration basin using a surface isolation flux chamber (hood), and (c) comparison of the modeled removal efficiencies with those measured to verify the model's accuracy.

Three compounds of interest to the pulp and paper industry were examined; chloroform, methanol and chlorophenolics. These compounds were selected to represent compounds believed to be removed during wastewater treatment primarily by only one mechanism; stripping, biodegradation or biosorption. The various chemical and biological parameters required to run the model were estimated from published values or published regressions with a surrogate parameter.

Removal Pathway	Rate Term	<b>Required Properties</b>
Stripping (Surface)	$r_{\rm S} = -K_L a * C_i$	Diffusivity in Water Henry's law constant
(Subsurface)	$r_{s} = -\frac{Q_{G}}{V}H * C_{i} (1-e^{-\theta})$	Air Flow $(Q_G)$
Volatilization	$r_V = -K_L^{v}a * C_i$	Molecular Weight Ambient Wind Speed
Biosorption	$r_a = -\frac{SP * K_p * C_i}{V}$	Partition Coeff. Sludge Prod. (SP)
Biodegrad.	$r_b = -k_2 * X * C_i$	Biodegrad. Rate Constant MLVSS (X)

#### **REVIEW OF THE FATE MODEL**

The NOCEPM model estimates the distribution of the fate of organic compounds influent to biological treatment. The model is based on (a) equilibrium relationships between the aqueous phase and the air and solid phases and (b) a second order biodegradation rate expression, coupled with the necessary terms defining hydraulic transport. The model is written for execution on personal computers and includes a data base containing the various chemical and physical properties required to simulate organic compound removal. The removal terms and required chemical and physical properties for each pathway are listed in Table 1. A detailed description of the model equations has been provided previously [1].

#### ANALYTICAL METHODS

During the historical loading phase of the study, volatile compound samples (chloroform and methanol) were collected as grab samples whereas the chlorophenolics were collected as 3 to 4 day composite samples. All aqueous phase samples collected coincident with the off-gas measurement were grab samples. Sample preservation was performed as follows: chloroform and methanol; pH = 5.0 with HNO<sub>3</sub> and chlorophenolics; pH = 2.0 with H<sub>2</sub>SQ<sub>4</sub>. All samples were cooled after collection and stored at 4°C until analysis.

Volatile Compounds—Aqueous phase chloroform was analyzed via the solvent extraction method developed by NCASI for pulp and paper wastewaters [2]. Further validation of this method is reported in a later NCASI technical bulletin [3]. Duplicate analyses were performed for all samples. The sorbent tubes, on which the samples of gas phase chloroform were collected, were analyzed via the procedure reported by NCASI [4].

Aqueous phase methanol samples were analyzed by direct injection of an aliquot of the sample into a gas chromatograph (GC) with flame ionization detection (FID). Silica gel sorbent tubes used for gas phase methanol sample collection were water

extracted and analyzed via the procedure of NIOSH method P&CAM 247 [5].

Non-Volatile Compounds—Aqueous phase chlorophenolics were analyzed by the revised gas chromatographic procedure NCASI Method CP-85.01 [6].

#### **DESCRIPTION OF TEST SITE**

Two criteria for selecting a test site were established for this study: (a) bleach kraft production with a hypochlorite stage in the kraft bleaching sequence and (b) subsurface aeration in the aeration basin. The former criterion was established because of the documented relationship between chloroform production and hypochlorite bleaching [3] while the latter criterion was needed in order to facilitate collection of aeration basin off-gases.

The host mill produces 630 tpd of bleached kraft (softwood and hardwood) and a total of 300 tpd of groundwood and thermomechanical pulp. The kraft pulp is bleached using a CEHD sequence with a moderate hypochlorite charge (approximately 13 percent) in the H stage.

Total mill effluent passes through a single primary clarifier the overflow of which, after the addition of supplemental nitrogen and phosphorous, flows by gravity to the activated sludge process. The activated sludge process consists of two approximately equally sized parallel aeration basins followed by three secondary clarifiers. A tracer study performed on one of the aeration basins, as part of this study, suggests that the flow split between the two basins may not be even. The total volume of the aeration basins is 33,500 m<sup>3</sup>. The aeration basins are equipped with a total of 2300 coarse-bubble diffuser units. Table 2 lists the pertinent operating parameters for the date of the off-gas sampling.

#### ORGANIC COMPOUND LOADINGS AND RE-MOVAL EFFICIENCIES

Secondary treatment influent and effluent concentrations

	Table 2 Operating	Parameters	at Test Site Wastewater Treatment Process		
Total Mill Flow:	1.18	m <sup>3</sup> /s	Aeration Basin MLSS:	3180	g/L
Pri Clar Infl BOD .:	359	mg/L	Aeration Basin Temp:	32	°C
Pri Clar Effl Temp:	32	°Č	Blower Horsepower:	4500	HP
Pri Clar Effl TSS:	188	mg/L	Blower Air Flow:	38.7	m <sup>3</sup> /s
Sec Clar Effl Temp:	28	°C	Return Sludge TSS:	8300	mg/L
Sec Clar Effl TSS:	64	mg/L	Return Sludge Flow:	0.96	$m^3/s$
Sec clar Effl BOD <sub>5</sub> :	22	mg/L	Wasted Sludge:	22,700	kg/day

Table 3 Results of Historical Loading and Effluent Concentrations—Volatile Compounds							
				Day			
Compound	1	4	8	11	15	18	Avg.
Chloroform (mg/L)							
Influent	1.35	1.42	0.84	1.30	0.73	0.91	1.09
Effluent	0.16	0.23	0.06	0.16	0.14	0.13	0.15
Percent Removal	88	84	93	88	81	86	86
Methanol (mg/L)							
Influent	93	80	53	92	75	84	80
Effluent	<1	<1	<1	<1	<1	<1	<1
Percent Removal	>99	>99	>98	>99	>99	>99	>99

for the three compounds were determined on a semi-weekly basis over a three week period (approximately five solids residence times) prior to the off-gas collection study. The resulting data not only establish a history of the overall removal attained by the treatment process but also provide a measure of the loading to which the biosolids in the system were exposed. This allows for an estimate of the biosorption to be calculated.

The results of the historical loading and removal data collection phase for the volatile compounds are listed in Table 3 and the chlorophenolics data are listed in Table 4.

#### **Estimation of Chlorophenolics Partitioning Coefficients**

An estimate of the partitioning of the chlorophenolics between the aqueous and biosolids phases can be made from the chlorophenolic overall removal data and the rate of solids losses from the treatment process. This assumes that all removal is achieved through adsorption onto the solids. Direct measurement of the solids loading (i.e. extraction of the compound from the solids) was not attempted because of lack of a verified protocol.

The partitioning coefficient,  $K_p$ , is estimated by calculating the mass of the compound removed (adjusted for mass sorbed onto effluent TSS) per mass of solids loss from the process (wasted plus effluent solids) and dividing by the effluent concentration. The calculation was performed for all chlorophenolics found to be present above the detection limit. Table 5 lists the resulting estimates of solids loading rates and partition coefficients.

For modeling purposes, it is desirable to relate the partitioning coefficient with a chemical property more readily available such as the compound's octanol-water partitioning coefficient,  $K_{ow}$ . Two such regressions are available from the published literature. Karickhoff *et al.* [7] provide the following regression (adjusted to units consistent with this paper) determined from adsorption of hydrophobic compounds onto natural sediments:

$$\log K_{oc} = 1.00 * \log K_{ow} - 3.21$$
 (1)

where;

- $K_{oc}$  = Partition Coefficient based on fractional organic carbon content of solids (L/gm)
- $K_{ow}$  = Octanol-Water Partition Coefficient of the compound (L/L)

The biosolids partition coefficient is then determined by:

$$K_p = f_{oc} * K_{oc} \tag{2}$$

where;

Table 4 Summary of Secondary Treatment Concentrations Objectmenters

 $f_{oc}$  = fraction of organic carbon in solids (gm/gm) Namkung and Rittmann [9] suggest that a value of 0.531 be assigned to  $f_{oc}$  based on a biosolids composition of  $C_5H_7O_2N$ .

	Average Influent	Average Effluent	Percent Removal
Compound	(µg/L)	<u>(μg/L)</u>	(%)
2,6-Dichlorophenol	ND	ND	
2,4-Dichlorophenol	3.7	0.8	78
2,4,6-Trichlorophenol	6.9	3.4	51
2,4,5-Trichlorophenol	ND	ND	_
2,3,4,6-Tetrachlorophenol	1.4	ND	100
Pentachlorophenol	ND	ND	-
4,5-Dichloroguaiacol	14.2	4.7	67
3,4,5-Trichloroguaiacol	17.0	13.7	19
4,5,6-Trichloroguaiacol	4.1	2.7	34
Tetrachloroguaiacol	8.7	4.1	53
3,6-Dichlorocatechol	0.2	ND	100
3,4-Dichlorocatechol	ND	ND	_
4,5-Dichlorocatechol	7.3	4.6	37
3,4,6-Trichlorocatechol	0.4	ND	100
3,4,5-Trichlorocatechol	17.5	6.5	63
Tetrachlorocatechol	11.1	4.6	59
6-Chlorovanillin	17.2	1.0	94
5,6-Dichlorovanillin	1.4	ND	100
Chlorosyringaldehyde	ND	ND	
Trichlorosyringol	3.1	3.0	3

Note: Removal percentage based on Average Influent and Average Effluent data.

Estimate	d Log	Calcula	tod Vn
			teu Kp
K <sub>p</sub> L/gm	Log K <sub>ow</sub> <sup>a</sup> L/L	M-M L/gm	Karick L/gm
7.99 3.07	3.21 3.75	0.35 0.80	0.53 1.84
5.92 0.67 1.62 2.99	3.18 4.11 3.74 4.45	0.33 1.39 0.79 2.35	0.49 4.21 1.80 9.21
1.60 4.68 4.23	N/A 3.79 4.19	0.85 1.58	2.02 5.06
		$\begin{array}{c c} & & & & & & \\ & & & & & & \\ \hline & & & & &$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Note: (a) From Reference [8]

The second regression is one developed by Matter-Muller et al. [10] using activated sludge. The regression, based on five compounds with log  $K_{ow}$  values ranging from 2.8 to 4.7, has the following form:

$$\log K_p = 0.67 * \log K_{ow} - 2.61$$
 (3)

Values of  $K_p$  determined from the measured influent and effluent data, based on equations (2) and (3) are also listed in Table 5. For both regressions, the measured  $K_p$  values for compounds with two chlorine substitutions greatly exceed values calculated by either of the regressions. It is likely that biodegradation of these compounds has occurred resulting in an over-estimation of the actual solids loading. Kincannon et al. [11] report that all of the 77 percent removal of 2,4dichlorophenol achieved in a bench-scale activated sludge reactor treating a combination of phenolic compounds was attributable to biodegradation while Banerjee et al. [12], using pure cultures, found that the rates of degradation of 2,4-dichlorophenol and 2,4,5-trichlorophenol were 530 and 20 times that of tetrachlorophenol, respectively. No data is available regarding the biodegradability of dichloroguaiacol.

The remaining six compounds display little correlation between measured and calculated  $K_p$  values. The Matter-Muller regression overestimates the measured  $K_p$  value for all compounds except 3,4,5-trichloroguaiacol, whereas  $K_p$  values predicted by the Karickhoff equation are apparently randomly distributed about the measured values. Biodegradation is believed not to be a factor in this case as Leuenberger *et al.* [13] found that the degree of sorption for 2,4,6-trichlorophenol and 4,5,6-trichloroguaiacol did not increase as a function of time, indicating biodegradation is minimal for these compounds. The error may be partially caused by estimating the solids phase concentration by a difference calculation rather than direct measurement.

## AERATION BASIN OFF-GAS COMPOSITION MEASUREMENT

This phase of the study involves direct measurement of volatile emissions from the aeration basin. The data collected reflect emission rates from a single basin at a single time and thus are intended to be used only for model verification rather than as an indication of typical volatile compound emission rates from the industry's wastewater treatment processes.

#### Materials and Methods

Hood Design—The hood constructed for collection of offgases is essentially identical to that designed and used by Bell et al. [14] in their study of off-gas emissions from Canadian municipal wastewater treatment processes. The hood was fabricated from 16 gauge aluminum sheets with the open bottom covering a  $1.2 \text{ m} \times 1.2 \text{ m}$  area. Off-gases exit the hood via a 8 cm diameter vent under which an aluminum plate was mounted to minimize foam carry-over into the vent. Flotation was provided by securing 20 linear feet of 10 cm plastic drainage pipe around the base of the hood. The hood design is displaced in Figure 1.

Off-Gas Sampling—Separate sampling trains for methanol and chloroform were used. Sampling traps were replaced every 40 minutes during the field test, capped and stored under chilled conditions until extracted in the laboratory.

Methanol was adsorbed from the off-gas onto a silica gel sampling tube used for workplace air monitoring by NIOSH Method P&CAM 247 [5]. The tube was mounted vertically at the center of the top of the vent with the off-gas pulled through the tube by applying a vacuum to the exit end of the tube. A critical orifice inserted between the sorbent tube and the vacuum pump restricted flow through the tube to 180 ml/min. The silica gel sampling tube contains a 700 mg adsorbing section and two 150 mg backup sections. The sections are desorbed separately with distilled water and analyzed by gas chromatography using a flame ionization detector.

Off-gas chloroform was collected by tapping 0.6 cm Teflon tubing into the side of the hood vent and connecting the tubing to the inlet of a sampling tube containing Tenax adsorbent. The Tenax tubes contain a primary section (2.1 gm Tenax TA 60/80 mesh) used for quantification and a secondary section (0.7 gm Tenax) to check for chloroform breakthrough from the primary section. Further description of the Texax tube design is provided in an earlier NCASI report [4]. The Texax tube outlet passes through a 180 ml/min critical orifice and then to the vacuum pump.

The temperature of the off-gas was measured by inserting a thermometer in the silica gel mount in the hood vent. A temperature of 17°C was measured for the off-gas. The ambient air temperature was  $-4^{\circ}$ C and the aeration basin liquid temperature was 32°C.



FIGURE 1. Schematic of off-gas sampling hood.

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FIGURE 2. Off-gas sampling locations in aeration basin.

Aqueous Phase Samples—All aqueous phase samples were collected as grab samples in this part of the study. Samples collected from the aeration basin were covered and allowed to settle for about five minutes prior to transfer to the sample jars. Although this removed the majority of the biosolids from the sample, in some cases there clearly were significant quantities of solids transferred to the sample bottle, perhaps as much as 200 to 300 mg/L.

Secondary clarifier samples were collected directly from the clarifier at a point approximately one-quarter of the length of the clarifier from the inlet. This location was selected as a trade-off between (a) achieving TSS reduction and (b) minimizing volatilization of compounds across the clarifier surface. The samples were covered and settled (two minutes) prior to transfer to sample jars.

#### **Off-Gas Hood Placement**

A hydraulic tracer study was performed on the aeration basin prior to the off-gas field test to determine appropriate locations for placement of the hood so that representative off-gases would be collected. It was desired to collect off-gases at multiple locations within the basin, one near the influent and one near the effluent, so that an average emission rate for the basin surface could be estimated. Furthermore, for logistical reasons, locations near the basin edge were preferred. Therefore, the objectives of the tracer study were to (a) establish the mixing regime of the basin so that the uniformity of emissions rates could be qualitatively estimated and (b) locate specific points near the basin edge which were in the primary flow pattern of the basin.

The tracer study concluded that (a) the aeration basin is a well mixed basin, but not completely mixed and (b) locations along the mid-feather separating the two aeration basins (termed the 'mid-point' locations) are in the primary flow pattern. The study also noted that because the basin is not completely mixed, basin contents at the mid-point location can be expected to have a higher concentration of volatile organics relative to the effluent location. The effluent location was selected as a point off the end of a pier extending approximately 3.7 meters out over the basin near the basin draw-off point. The two hood locations used are displayed in Figure 2.

At both locations, the surface boil created by air released from an individual diffuser was selected for placement of the hood. The dimensions of the hood were such that it extended over an area believed to be impacted by a single diffuser.

#### **Results of Off-Gas Field Test**

Aqueous Phase Samples—Concentrations of the volatile compounds measured at secondary influent, the off-gas hood location and secondary effluent are listed in Table 6. The data represent average values determined from three samples collected during the period when the hood was positioned at the mid-point location and two samples collected when the hood was positioned near the aeration basin effluent. The influent samples were collected at the beginning of the 40 minute intervals during which off-gas sorbent tubes were on-line and the hood location and secondary effluent samples were collected at the mid-point of the test intervals.

The influent and effluent data during the off-gas test are consistent with those data collected during the historical loading phase of the study suggesting that the loading and operational conditions during the field test were normal for the host mill. Comparison of the aqueous samples collected at the two hood locations shows that while the majority of the overall removal has occurred at the mid-point (78% and 94% for chloroform and methanol, respectively) a concentration gradient exists in the basin and therefore a gradient in off-gas emission rates would be expected.

It should also be noted that a slight decrease in chloroform concentration occurs between the sample collected at the aeration basin effluent and that collected in the secondary clarifier. This probably occurs as the result of volatilization from the clarifier headbox, which is fairly turbulent, or as the result of mixing with the effluent of the other aeration basin which could possibly have a higher chloroform concentration.

Table 7 lists the aqueous phase data collected during the offgas test for the chlorophenolics. Here again, secondary influent

Table 6 Results of Aqueous Samples During Off-Gas Field Test—Volatile Compounds						
Compound	Units	Secondary Influent	Hood Location	Secondary Effluent		
MID-POINT LOCATION:						
Chloroform	mg/L	1.03 (0.95–1.08)	0.34 (0.32–0.35)	0.14 (0.14–0.14)		
Methanol	mg/L	97 (90–108)	4.3 (1.8-6.1)	<1 (<1 - <1)		
EFFLUENT LOCATION:						
Chloroform	mg/L	1.00 (0.98–1.01)	0.19 (0.19–0.19)	0.14 (0.14–0.14)		
Methanol	mg/L	100 (97–103)	<1 (<1 - <1)	<1 (<1 - <1)		

Notes: 1) Numbers in parentheses represent range of results.

Table 7 Re	Table 7 Results of Aqueous Samples During Off-Gas Field Test—Chlorophenolics						
	Infl	Influent		Hood Loc.		Effluent	
Compound	<u>A*</u>	<u> </u>	<u>A</u>	B	<u>A</u>	В	
2,6-Dichlorophenol	1.0	ND	ND	ND	ND	ND	
2,4-Dichlorophenol	4.9	4.1	3.0	3.4	1.2	2.5	
2,4,6-Trichlorophenol	7.2	7.0	4.9	5.8	4.2	5.0	
2,4,5-Trichlorophenol	ND	ND	ND	ND	ND	ND	
Tetrachlorophenol	1.0	1.5	ND	ND	ND	ND	
Pentachlorophenol	ND	ND	ND	ND	ND	ND	
4,5-Dichloroguaiacol	12.9	10.9	3.7	4.4	3.0	3.2	
3,4,5-Trichloroguaiacol	15.9	18.9	23.2	36.4	13.0	13.6	
4,5,6-Trichloroguaiacol	4.2	4.1	2.3	4.7	2.8	2.9	
Tetrachloroguaiacol	6.8	8.7	4.3	5.4	3.9	4.3	
3,6-Dichlorocatechol	ND	1.7	ND	ND	ND	ND	
3,4-Dichlorocatechol	ND	ND	ND	ND	ND	ND	
4,5-Dichlorocatechol	8.2	7.2	19.7	22.2	5.9	6.3	
3,4,6-Trichlorocatechol	1.2	1.2	ND	1.2	ND	ND	
3,4,5-Trichlorocatechol	22.3	21.1	26.4	37.2	8.9	9.7	
Tetrachlorocatechol	13.3	12.7	6.8	8.3	4.8	5.2	
6-Chlorovanillin	17.7	15.5	4.7	3.9	ND	ND	
5,6-Dichlorovanillin	7.4	6.0	ND	ND	ND	ND	
Chlorosyringaldehyde	1.0	ND	ND	ND	ND	ND	
Trichlorosyringol	1.0	3.3	3.3	3.8	2.9	2.8	

Notes: All data expressed as µg/L

(\*) A = Mid-Point Location; B = Effluent Location

ND = Not Detected

and effluent data are consistent with the historical loading data. Only the influent average for 5,6-dichlorovanillin falls outside of the range measured during the historical loading period and, in most cases, both the influent and effluent data averages are close to the averages determined during the historical loading period.

For several of the chlorophenolics (3,4,5-trichloroguaiacol, 4,5-dichlorocatechol and 3,4,5-trichlorocatechol), the concentration measured in the aeration basin is greater than that measured in the influent to the basin, particularly for aeration basin samples collected near the effluent. A possible explanation for this is the carry-over of biosolids, with these compounds adsorbed to their surface, from the aeration basin to the sample bottle. However, this does not explain why similar results are not observed for other compounds with even larger partitioning coefficients such as tetrachloroguaiacol and tetrachlorocatechol.

Off-Gas Samples—Table 8 lists the mass of chloroform and methanol sorbed on the Tenax and silica gel traps, respectively, for each of the test intervals. The test intervals consisted of three consecutive 40 minute periods at the mid-point location and two consecutive 40 minute periods at the basin effluent location. A period of about 1 hour elapsed between completion of the mid-point test and initiation of the effluent test.

In two of the five Tenax traps, chloroform was detected in the secondary section of the trap but only at levels representing approximately one percent of the mass in the primary section. The other three secondary sections were found to have no detectable chloroform. The reproducibility of the off-gas chloroform data was excellent; variability about the mean chloroform mass was less than ten percent. Furthermore, the anticipated gradient in off-gas composition was observed; the chloroform mass trapped at the midpoint location was 37 percent more than that trapped at the effluent location over the same sampling duration.

Methanol was only detected in one of the silica gel tubes. At this time, it is not clear whether the off-gas contained only very low concentrations of methanol or if condensation which collected in the silica gel tubes during sampling inhibited methanol sorption. The NIOSH method description indicates that condensation in the tube can be an interference [5]. Future field tests with the hood will attempt to prevent condensation by (a) conducting tests at warmer ambient temperatures and (b) warming the silica gel tube during the test.

The apparent absence of methanol in the off-gas is contra-Table 9 Mass Balance of Chloroform Around Aeration

Table 8 Results of Analysis of Off-Gas Samples Collected Over Aeration Basin				
Sampling	Chloroform		Methanol	
Interval	μg	ppm-v	μg	
MID-POINT LOCATION:				
I	228		<3	
II	211		147	
III	190		<3	
Average:	210	5.5		
EFFLUENT LOCATION:				
IV	137		<3	
v	166		<3	
Average:	153	4.0		

Basin		
Location	Chloroform kg/d	
Secondary Influent	103	
Aeration Basin Off-Gas:	97	
Mid-Point Location	71	
Effluent Location Average	84	
Secondary Effluent	14	
Total Export (Off-Gas + Effluent)	98	

Table	10 Comparison of Measured and	d Predicted Removal Per	centages-Volatile Comp	ounds	
	Chlore	oform	Methanol		
Pathway	Measured (%)	Predicted (%)	Measured (%)	Predicted (%)	
Stripping	81	79	<1	<1	
Volatilization	_	1	-	0	
Sorption	_	<1	_	0	
Biodegradation	5	8	>99	97	
Effluent	14	12	<1	3	

dictory to measurements made by Thibodeaux *et al.* [15] above aerated stabilization basins treating bleach kraft mill effluents. Based on an average methanol emission rate of 1.2 kg/ton pulp reported by Thibodeaux, a mass of 1.7 mg would be expected on the silica gel tube. Although the emission rate of a compound with a volatility on the order of methanol from a basin equipped with diffused aeration is expected to be significantly less than that from basins with surface aerators, based on Thibodeaux's data it was anticipated that a methanol mass much greater than the detection limit of 3  $\mu$ g would be collected on the silica gel.

#### Calculation of Emission Rates

The concentration of chloroform in the off-gas was calculated by dividing the moles of chloroform sorbed to the trap by the number of moles of air passed through the trap. This data is listed in Table 8 in units of ppm-v. These concentrations are then multiplied by the molecular weight of chloroform and the total moles of air supplied to the aeration basin diffuser system (estimated from blower capacity) to determine the total emission rate at that location. Table 9 presents the results of this calculation as well as the chloroform mass at the secondary treatment influent.

Chloroform data listed in Table 9 indicate excellent mass balance with only five percent of the influent chloroform unaccounted for. This difference could be the result of biodegradation of the influent chloroform or is simply within the expected error band associated with sampling and analysis.

#### **MODEL VERIFICATION**

The NCASI organic compound removal model was used to simulate the removal of the compounds under study. Data collected during the day of off-gas sampling was used for simulating chloroform and methanol removal, whereas, the historical loading data was used for simulating chlorophenolics removal because of the anticipated dominance of biosorption as the removal mechanism for these compounds. The two chlorophenolics, 3,4,5-trichloroguaiacol and tetrachloroguaiacol, were selected because of their relatively high concentration in the influent and because of the availability of partitioning coefficients from the literature.

#### **Model Inputs**

Model inputs relating to treatment process description were obtained from Table 2. In addition, a standard oxygen transfer efficiency of 1.14 Kg oxygen/horsepower/hour and an ambient wind velocity of 2 m/s were assumed. Biodegradation rate constants were selected based on assumed relative biodegradability and experience with using the model. Methanol was assigned the highest biodegradable rate used in the model, chloroform was assigned a value indicative of low biodegradability and the chloroguaiacols were assigned biodegradability values approaching zero.

#### **Comparison With Measured Data**

Table 10 compares predicted pathway specific removals with those measured in the field study for chloroform and methanol. Entries for measured biodegradability in Table 10 are based on the difference between influent mass and total measured export mass and potentially include removal via sorption, although the extent of sorption actually occurring is expected to be minimal. For both chloroform and methanol, the model predicts removal attributable to the primary removal pathway (stripping for chloroform, biodegradation for methanol) to within two percent of that measured. Overall removal is also predicted to within two percentage points of that measured. Note that the predicted effluent entries include the aqueous phase concentration plus any mass of the compound which may be sorbed to solids in the final effluent stream.

Measured and predicted removals for 3,4,5-trichloroguaiacol and tetrachloroguaiacol are compared in Table 11. Agreement is obtained to within 4 percent of that measured for 3,4,5-trichloroguaiacol. The model underestimates the measured removal of tetrachloroguaiacol by a margin of 19 percent. The latter is a result of the solids partitioning coefficient,  $K_p$ , calculated from the compound's octanol-water partition coefficient being lower than that estimated from the measured tetrachloroguaiacol overall removal data.

#### CONCLUSIONS

This paper reports the results obtained for an initial study of the removal pathways of various compounds during wastewater treatment and the accuracy of the NCASI organic compound removal model for predicting these removals. Further study is needed to address such issues as; (a) determination of biodegradation and biosorption parameters through laboratory experimentation and (b) variability of removal rates for a given system and for the industry as a whole. Bearing this in mind, the following conclusions can be drawn from this study for the diffused-aeration activated sludge basin examined:

(1) Forced stripping by the aeration system is the predominant removal pathway for chloroform. Furthermore, chloroform emission rates to the atmosphere represent approximately 80 percent of the influent chloroform mass.

	Table 11 Comparison of Measu	red and Predicted Remova	I Percentages—Chlorogua	iacols
	3,4,5-Trichl	oroguaiacol	Tetrachloroguaiacol	
Pathway	Measured (%)	Predicted (%)	Measured (%)	Predicted (%)
Overall	19	23	51	32

(2) Biodegradation is the predominant removal pathway for methanol and overall methanol removals greater than 99 percent were consistently achieved.

(3) Overall removals for the chlorophenolics ranged from nearly zero (trichlorosyringol) to greater than 99 percent with a mean of 58 percent. Solids partitioning coefficients calculated as the mass of compound removed per available solids (wasted plus effluent) were generally greater than that predicted from two regressions available from the literature, particularly for the lower chlorine substituted compounds. If the literature equations are correct, this indicates that these compounds are potentially biodegraded within the treatment process.

(4) Comparison of predicted removal percentages with measured data indicates that the NCASI organic removal model predicts removal via the predominant pathway and overall removal to within two percentage points for chloroform and methanol. Close agreement was obtained for 3,4,5-trichloroguaiacol (to within 4 percent) although the model underestimated the measured removal of tetrachloroguaiacol by a 19 percent margin.

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## Competitive Sorption of Benzene, Toluene and The Xylenes onto Soil

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Knowledge of contaminant soil-groundwater partitioning is of crucial importance in determining contaminant transport. The majority of studies to date examine only single contaminant partitioning. Studies presented in this paper investigated single contaminant and multiple, competitive contaminant partitioning of benzene, toluene, and xylenes with a sandy loam soil. Batch serum bottle and flow soil column studies were utilized. Significant competitive effects were observed.

#### **PROBLEM STATEMENT**

Evaluation and remediation of the impact that hazardous chemicals have on the quality of groundwater has been identified as a high priority in the State of New Jersey and the United States. Recent testing of public water supplies revealed that among the most frequently observed contaminants were benzene, toluene, and the xylene isomers (BTX) [J]. These monoaromatic hydrocarbons are common constituents of fuels and solvents, and through the processing, handling, and storage of these products, BTX have contaminated soils and groundwater. As major components of unleaded gasoline, BTX has a ubiquitous presence throughout much of the world. Leakage from storage tanks has been identified as a primary source of soil and water contamination [2].

These volatile organics pose a serious health threat even at very low levels. Although the toxicity of BTX is not completely understood, the benzene concentration in drinking water as sumed to cause a one in one million increased lifetime cancer risk is  $0.67 \ \mu g/L$  [3]. For this reason, environmental regulations have mandated the reduction of these compounds within soil and groundwater systems. Knowledge of the fate of these compounds in soils and aquifers is of critical importance to the design of effective monitoring and remediation processes. Modeling of the fate of BTX in soil and groundwater systems and the development of treatment processes, rely strongly on knowledge of the transport properties of the species which are present in the matrix of interest. Therefore, the interaction between the BTX and soil and groundwater systems must be determined so that adequate treatment and transport models may be developed.

#### **OBJECTIVES**

The goal of this work is to quantify the competitive effects of multiple contaminants on partitioning of BTX species between soils and groundwater. The majority of adsorptiondesorption studies to date have investigated single contaminant interactions with soils [4,5,6,7,8,9]. Preliminary data obtained recently suggests that competitive effects on soil-groundwater partitioning can be very significant [10].

Quantification of competitive effects for this work has been accomplished through use of batch adsorption studies comparing single component partitioning to multi-component partitioning. Soil column experiments were utilized to verify batch results with continuous flow systems. Utilizing this experimental data, a numerical model was developed in order to simulate contaminant transport through the soil column. Parameters which were needed to properly delineate the problem included dispersion and partitioning coefficients.

The specific objectives of this research investigation were fourfold. The first objective was to determine a dispersion coefficient which accurately describes the mixing effects of flow through the soil columns. The second objective was quantification of single species partitioning using batch studies and to compare these results with observed effects in flow systems. The third objective was quantification of the competitive effects of multiple species partitioning in batch studies. Finally, these effects were combined experimentally in the soil column systems and a numerical model of the combined transport properties of BTX in flow systems was developed.

First place winner of the 1990 Environmental Division Student Paper Competition

Table 1 Soll Characteristics for Adelphia Sandy Loar (all percentages are by weight)			
Moisture Content	"as is" air dried oven dried	5-30 % 1-3 % 0 %	
Particle Size	Sand Silt Clay	70 % 12 % 18 %	
Organic Matter		1.07 %	
Organic Carbon		0.62 %	
Surface Area (BET)		13.1 m <sup>2</sup> /gm	
Cation Exchange Capacity		6.6 meq./100 gm	

#### **EXPERIMENTAL METHODS**

#### **Batch Sorption Isotherms**

Batch serum bottle studies were used in the determination of the individual (non-competitive) partitioning coefficients of the BTX species. Five 125 ml serum bottles were prepared for each of five concentration levels of each contaiminant. Three replicates of each mass level of contaminant were prepared with a measured mass of uncontaminated oven dried soil and a measured mass of water. The remaining two serum bottles (controls) for each mass level were prepared with only the contaminant and the water. Contaminant levels chosen were 3, 6, 30, 60, and 150  $\mu$ g/g (ppm) initial solution concentrations. All experimental units were completely sealed with septa and crimp tops after preparation, and extreme care was taken throughout the experiments to minimize volatility losses. The soil used for serum bottle studies, as well as the column experiments, was a sandy loam obtained from the Cook College Agricultural Station in Adelphia, New Jersey. The soil was air dried and then seived through a 16 mesh screen (1.18 mm). For the batch isotherm studies, the soil was further dried in an oven at 105°C for 24 hours. Some common properties for the soil which was used are listed in Table 1.

For the competitive adsorption studies, the serum bottles were prepared in the same manner as in the single contaminant studies. However, all five BTX components were injected into the serum bottle at the same time. The total contaminant concentration was equivalent to that of the single species (i.e., concentrations of 0.6, 1.2, 6, 12, 30  $\mu$ g/g for each species).

After sealing, the bottles were placed on an oscillatory shaker for 72 hours, removed, and allowed to settle. After this time, two equal volume pentane extractions were made from the aqueous phase of each serum bottle. A 2.5 ml liquid sample was injected into a 5 ml vial contain 2.5 ml of n-pentane (water immiscible). The BTX was extracted into the pentane phase due to its affinity for the organic solvent and the extract concentration was quantified in duplicate runs on a gas chromatograph (GC) (see Analytical Methods).

#### Soil Column Studies

The experimental apparatus used to carry out the flow experiments is illustrated in Fig. 1. It consisted of heavy-wall glass columns with an inner diameter of 3 inches and a length of 30 inches. Sampling ports were installed every 5.75 inches along the length of each vertical column. A nutrient addition port was installed at the base of the column so that subsequent experiments could examine biological activity utilizing the same apparatus. Uncontaminated soil was packed in layers of 5.5 inches in tandem with 0.25 inches of 2 mm glass beads which were located at the sampling port levels. The purpose of the glass beads was to provide sufficient void volume from which to draw a sample. A teflon tube was inserted into the center of the glass beads so that samples extracted would be indicative



GLASS BEADS C SAMPLING PORTS O . PORT NUMBER

FIGURE 1. BTX column design.

of the local composition at that level. Columns were run in duplicate based on the conditions under which the studies were carried out.

Contaminated water feed was pumped, using a cassette pump, through the base plate in an upflow manner to provide a uniform flow pattern. The flow rate to each of the columns was approximately 200 ml/day (pore velocity of 10.47 cm/ day) which typifies probable field conditions. The average daily flow which was used in the numerical model was obtained by dividing the observed total weekly flow into equal daily rates. Influent contamination levels were maintained in the 15-20 $\mu g/g$  range and were monitored by weekly sampling of the feed bag. The effluent liquid was allowed to pass through a gas separation tube, where any product gas could be collected, and dispensed into a graduated liquid collection bottle. Each of the sampling ports were sampled on a weekly basis and quantified by GC analysis using pentane extractions.

#### **Analytical Methods**

The concentration of BTX in aqueous solution was determined by pentane extraction followed by gas chromatography. A Hewlett Packard 5890 GC with a 5895A Chemstation and a 7673A Autosampler was used. The samples were injected onto a 5% SP-1200/1.75% Bentone 34 on 100/120 Supelcoport column (Supelco, Bellefonte PA) which was 6 feet by .125 inch in accord with EPA Method 602. Quantification was by photoionization detection (PID) (HNU Systems-Model PI-52-02A) with helium as carrier gas at a flow rate of 30 ml/min. The analysis was run isothermally at 70° C. Three external standards were run at the beginning of each set of samples.

Analysis of chloride concentration was by use of a chloride anion selective probe (Orion). The probe generates a millivolt signal which is converted to concentration by a logarithmic function. A standard curve was generated by using three point calibration on solutions of 10, 100, and 1000 mg/L.

#### NUMERICAL MODELLING

Transport of BTX in soil columns is the result of four major competing processes: dispersion, convection, sorption, and biodegradation. Biological effects were minimized through lack



FIGURE 2. Chloride study column No. 1.

of nutrients and co-substrate necessary for microbial activity. Equation 1 shows a rate equation in which the change in concentration (c) with respect to time (l) is a function of these three effects [11]. The first term involves the dispersive effects  $(E_z)$ , the second term involves convective effects  $(u_p)$ , the third term accounts for biodegradative effects  $(K^*)$ , and all three involve sorptive effects through the retardation factor  $(R_c)$ .

$$\frac{\partial c}{\partial t} = \frac{E_z}{R_c} \left( \frac{\partial^2 c}{\partial z^2} \right) - \frac{\overline{u}_p}{R_c} \left( \frac{\partial c}{\partial z} \right) - \frac{K^*}{R_c} c \tag{1}$$

The retardation factor is a measure of contaminant partitioning between soil and water phases, during flow through the columns, and is expressed as:

$$R_c = 1 + (\rho k' / \theta_s) \tag{2}$$

where  $\rho$  is the soil density (g/cm<sup>3</sup>), k' is the partitioning coefficient (dimensionless), and  $\theta_s$  is the moisture content of the soil (g/cm<sup>3</sup>).  $R_c$  is dimensionless.

With the biological effects minimized, a classic explicit finite difference approximation was applied to the rate equation. The resulting expression,

$$c_{i+1,j} = \left(\frac{2E_{z}h + \overline{u}_{p}hk}{2R_{c}k^{2}}\right)c_{i,j-1} + \left(\frac{R_{c}k^{2} - 2E_{z}h - k^{2}K^{*}h}{R_{c}k^{2}}\right)c_{i,j} + \left(\frac{2E_{z}h - \overline{u}_{p}hk}{2R_{c}k^{2}}\right)c_{i,j+1} \quad (3)$$

utilizes forward finite differences with respect to time (i), and central finite differences with respect to space (j) for accuracy







FIGURE 4. Chloride tracer study model.

of approximation. The stability of the approximation is assured if the step sizes (*h*-time, k-space) meet the following criteria [12]:

$$h < \frac{R_c k^2}{2E_z + k^2 K^*} \quad \text{(time)} \tag{4}$$

$$k < \frac{2E_z}{\overline{u}_p}$$
 (space) (5)

The resultant series of equations were solved using a FOR-TRAN program which permitted the calculation of predicted effluent concentrations. Used in tandem with spread sheet analysis, a graphical concentration profile was generated.

#### **RESULTS AND DISCUSSION**

To determine the dispersion coefficient, a step change in the chloride concentration of the column feed was employed. Chloride ion was chosen because, as an anion, it is repelled by the natural negative charge of the soil matrix and, therefore, is not sorbed. This is equivalent to zero partitioning, or a retardation factor equal to 1. The solution fed to the columns consisted of a 500 mg/L of magnesium chloride. At time zero, the influent concentration was increased to 1000 mg/L. Samples were taken at time zero, and subsequently at eight hour intervals. A concentration profile of replicate columns is provided in Figures 2 and 3. The variables in the model were regressed until an effluent profile which was similar to the data was generated (Figure 4). The dispersion parameter  $(E_2)$  was in units of cm<sup>2</sup>/day and the pore velocity  $(u_p)$  was in units of



FIGURE 5. BTX concentration in column 5.


FIGURE 6. BTX adsorption on soil. Batch non-competitive adsorption.

cm/day; both were assumed to be constant over the nine day sampling period.

The next step involved utilizing water contaminated with BTX as the feed solution for the soil columns. A known quantity of each compound was injected into the feed and allowed to flow through the column. Thus, the influent for each column included a target concentration of 20  $\mu$ g/g benzene, 18  $\mu$ g/g toluene, 17 µg/g o-xylene, 16 µg/g p-xylene, and 15 µg/g mxylene. Samples were taken from the top port only (hereafter termed effluent) on a weekly basis. Effluent concentration profiles are provided for benzene and the xylenes in Figure 5. Toluene data showed a decrease in concentration which was not typical of the other components or the predicted response. The cause has not yet been determined, but the possibilities include both abiotic and biological means. It was therefore decided that the toluene data will not be presented. In order to generate a model of the profiles for benzene and the xylenes, partitioning coefficients needed to be determined for each of the BTX components.

The partitioning coefficient for a given compound can be represented by the slope of a line through the plot of the soil phase concentration versus the aqueous phase concentration. The necessary mass ratios were determined based on GC analysis of the samples generated in the batch single component adsorption studies. The difference in concentration in the aqueous phases of the two treatments, soil versus no soil, is assumed to be the amount of contaminant which partitioned into the soil. The graphical results can be seen in Figure 6. The  $R^2$  value of these slopes were all between 0.90 and 0.99.

These coefficients, along with experimental values for soil density ( $\rho = 1.31$  g/cm<sup>3</sup>) and moisture content ( $\theta_s = 0.276$  g/cm<sup>3</sup>), were used in the calculation of  $R_c$ . With this value, and the dispersion and pore velocity obtained earlier, a predicted







FIGURE 8. m-Xylene concentration vs. time. Experimental data and model (Rc = 6.26).

effluent profile was generated (Figure 7). Upon inspection, the first discrepancy noticed was that the model predicted a smooth sigmoidal curve. This was not the case for the experimental data (Figure 5). This led to the hypothesis that any influent flux variation in flow rate or contaminant concentration greatly affects the form of the effluent profile. The FORTRAN program was modified to account for the variance in volumetric flow and contaminant level on a weekly basis. The modified program predicted a profile which was much more irregular. as seen in Figure 8. However, as shown, the breakthrough time (time at which the concentration level increases from zero baseline) was predicted to be much longer than observed experimentally. This meant that the retardation factors in the actual flow system were less than the ones used in the model. Since the density and moisture content are characteristic properties for a given soil system, the partitioning coefficient could be the only erroneous variable used in calculation of the retardation factor. Values were needed which would describe a



FIGURE 9. BTX adsorption on soil. Batch competitive adsorption.

Table 2 BTX	Partitioning C	oefficients in So ms	il/Water Sys-
Compound	Individual	Competitive	% Change
Benzene	0.11	0.21	+91%
Toluene	0.16	0.14	-13%
m-Xylene	1.11	0.53	- 52%
o-Xylene	1.45	0.46	- 68%
p-Xylene	0.67	0.53	- 21 %



FIGURE 10. Benzene concentration vs. time



FIGURE 11. m-Xylene concentration vs. time. Experimental data and model (Rc = 3.49)

system where competitive adsorption existed between multiple species.

The results seen in Figure 9 show the competitive adsorption isotherms. The  $R^2$  values for these coefficients were between 0.91 and 0.97 (with the exception of toluene at 0.84). These results indicated that there is a significant decrease in the affinity that the contaminants have for the soil when in a competitive environment. The magnitudes of the partitioning coefficients for the xylenes were affected the most, with changes of up to 68% (Table 2).

Incorporating the competitive partitioning coefficients and the variable influent fluxes into the model, effluent concentration profiles were generated which much more accurately predicted the observed effluent profiles and breakthrough times (Figures 10-13).

### CONCLUSIONS

It has been shown that the competitive effects for sorptive partitioning are extremely significant. In systems where more than one of the BTX species are present simultaneously, the single component adsorption data is not a good predictor of BTX transport rates. This can have large effects on the prediction of the transport of contaminants at sites where multiple species are present. The lowered affinity for the soil in competitive situations allow the contaminants to move more quickly through the soil system. This results in a considerable under estimation in the rate of contaminant transport.

This work has also proven that batch isotherm data can be used to accurately predict competitive sorptive behavior in flow systems. This is vital in the respect that in order to predict the



FIGURE 12. o-Xylene concentration vs. time. Experimental data and model (Rc = 3.15).



FIGURE 13. p-Xylene concentration vs. time. Experimental data and model (Rc = 3.5).

transport response of contaminants in field conditions, predictive laboratory data is needed to simulate a naturally occurring environment.

### ACKNOWLEDGMENT

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# Alternative Waste Minimization Analyses for the Printed Circuit Board Industry: Examples for Small and Large Manufacturers

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The objective of the present waste minimization study for printed circuit (PC) board manufacture is to evaluate solid/liquid separation technologies, engineering data, waste recycling processes, and cost economics to assess the feasibility of achieving significant reduction in the usage of water, the generation of wastewater, and hazardous wastes. Two examples, for small and large manufacturers, demonstrate that an integrated waste minimization scheme can minimize waste by in-process recycling, resource recovery, process modification, and automation. Economic analyses of these two examples show that the integrated waste minimization scheme is more profitable than that of the conventional sludge or the "zero sludge" schemes.

### INTRODUCTION

The production processes of the printed circuit board manufacturing industry are similar to those of the electroplating and metal finishing industries. More than twenty steps are generally required to process a PC board, such as board preparation, board cleaning, surface preparation, catalyst application, electroless plating, image transfer, electroplating, soldering, etching, rinsing, etc [1-3, 15, 16].

Organic solvents are used for board cleaning and for the developing and stripping of photoresist materials in the image transfer process, such as methylene chloride, tricholoroethane, freon, etc. The metals, silver, gold, copper, tin, and their alloys are utilized because of their high conductivity, and thus their use in leads and connectors keeps power loss to a minimum. Table 1 lists examples of chemicals used in the PC board industry. The first major source of these inorganic and organic chemicals that are introduced into the waste stream results from the disposal of the spent plating baths and rinses directly following the plating process. The second major source of metallic contaminants is the chemical etch step utilized as part of the plating preclean operations or in the removal of excess surface metal. Etch rinses will also contain high concentrations of metals along with dilute levels of etching solution.

Typical hazardous waste streams generated by plating related processes are waste rinsing water, waste sludge, spent process baths, waste acids and bases used for board cleaning or etching, and metals salts. More than 60 percent of hazardous waste from PC board production line are in liquids with metals [3]. As effluent discharge limits for the electronics industry have become increasingly strict, the industry has been forced to treat wastewaters to remove dissolved metals. Since disposal of these sludges in landfills may be banned, other nonsludge-generating methods of management will see increasing utilization. Onsite waste reduction technologies are perceived as achievable and profitable methods to treat manufacturing wastes.

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### Table 1 Chemicals Used in Printed Circuit Board Industry

Process step	Chemicals	
Board Cleaning and Preparation	Na <sub>2</sub> CO <sub>3</sub> , NaOH, NaF, HCl, H <sub>2</sub> SO <sub>4</sub>	
Board Catalyzing	PdCl <sub>2</sub> , SnCl <sub>2</sub> , Cd	
Electroless Plating	CuSO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> O <sub>2</sub> , EDTA, HCHO	
Copper and Tin/Lead	$CuSO_4$ , $H_2SO_4$ , $Cl$ , $Cu$ , $Sn(BF_4)_2$ ,	
Electroplating	Pb(BF <sub>4</sub> ) <sub>2</sub> , HBO <sub>2</sub>	
Etching, Developing,	KOH, H <sub>2</sub> SO <sub>4</sub> , NH <sub>4</sub> Cl, NaClO <sub>2</sub> , HCl,	
and Stripping	Methylene Chloride, TEA	

Some of the methods for onsite minimization of the quantity of hazardous sludge include evaporation (EV), reverse osmosis (RO), ion exchange (IX), electrolytic cell (EC), electrodialysis (ED), ultrafiltration, extraction, activated carbon adsorption, etc. These techniques have already been used in some of the electroplating and metal finishing industries [4-7, 12-14]. Other techniques, such as material substitution, multi-stage rinsing, drag-out reduction, etc., also have been used by electroplating and metal surface finishing industries. An effective multi-stage rinsing system can reduce the water usage and the wastewater generation substantially. Consequently, the waste treatment cost can be reduced also.

### WASTE REDUCTION FOR PRINTED CIRCUIT BOARD INDUSTRY

Several waste reduction studies and economic analyses have been produced for the printed circuit board manufacturing industry [1-3, 8, 15, 17, 35].

One study [1] examined three waste treatment cases of three PC board manufacturers: two of them adopted the conventional precipitation waste treatment method, and the third uses a two-stage rinse system to reduce the water usage and applies a filtration, ion-exchange, and neutralization system to treat the effluent from rinse system. However, none of these three processes recycles rinse water.

Nunno et al. [2] studied waste water and solvent treatment for six PC board manufacturers or related businesses. They found that two (Facilities A and B) utilize the sodium borohydride precipitation method to treat their waste stream. They have extended the unit processes to include sodium hypochlorite oxidation of cyanides, sodium hydroxide precipitation, sodium borohydride reduction, filtrations, and ion exchange.

Facilities C and D recover solvents from photoresist stripping and developing processes with distillation and evaporation units. A flash evaporator is used to recover used methyl chloroform, a distillation column is applied to recover freon, and a box distillation unit is installed to recover methylene chloride from its waste streams. The total solvent recovery is 99.8%. However, for both facilities, the still bottoms containing trichloroethane, classified as hazardous waste, must be sent out for further treatment.

Facility E uses an activated carbon adsorption and filtration system to treat its spent plating solutions. Hydrogen peroxide is added to oxidize volatile organic species. The builtup organic contaminants are adsorbed by activated carbon. The solid particles are filtered, and the recovered bath is returned to the process. Facility F applies several electrolytic cells to recover copper and tin/lead from waste rinse water. The efficiency of recovery of copper is about 90%; however, recovery of tin/ lead is not effective.

Another study [3] has examined waste treatment for three PC board manufacturers. The study shows that the first manufacturer uses an ion-exchange system to treat and reuse 50% of total waste rinse water. Another 50% of waste water, which is combined with the regenerated streams, is discharged. The copper concentrated solution in drag-out tanks of this man-

ufacturer is treated separately with an aluminum chip precipitation method. The second manufacturer uses two electrolytic cells to recover metals from copper and tin/lead concentrates; however, the conventional precipitation method is also applied to treat dilute rinse streams and no rinse water is reused. The third manufacturer uses the conventional sodium hydroxide/ calcium chloride precipitation method to treat wastewater. Part of the rinse water was reused by the manufacturer.

Higgins [8] reviewed one PC board manufacturing waste minimization project. To minimize hazardous waste, this system treated the mixed waste rinse water by chelating ion exchange. They found that chelating ion exchange resins can sufficiently remove copper from the complexing agents, and allow the complexing agents to pass through to the effluent. Resins are then regenerated to produce a mixture of sulfuric acid and copper sulfate, which is then treated in an electrolytic cell to recover copper. However, instead of recycling the treated rinse water, it is discharged to the publicy owned treatment facility.

Moleux [15] has shown that it is possible to apply an electrolytic cell to treat the effluent (in which the copper concentration is 1.0 g/l) from a drag-out tank (following a microetching bath). A parallel-plate electrolytic cell can recover about 75% of copper from the effluent, but if a high surface area expanded mesh cathode system is used, more than 99.9% of copper can be recovered.

Hewlett Packard (HP) [17] has also applied an ion-exchange plus electrolytic system to treat its waste streams and to remove metals (copper and nickel) from waste rinse water and spent solutions. Metal reductions of copper and nickel in effluents are 99.96% and 99.6%, respectively.

From the above case studies, it is determined that:

- the conventional precipitation methods are still the main technology used by the printed circuit board industry; however, the removal efficiencies of different metals with these methods vary case by case;
- at least seven cases mixed their waste rinse streams before treatment, which will influence the efficiency and treatability of the waste treatment process;
- (3) only one or two cases applied drag-out control and multi-stage counter-current rinse technologies to reduce water usage and waste generation; and
- (4) among the above fifteen case studies, only two considered recycling or reducing their rinse water.

From these observations, it is apparent that an integrated waste minimization method should: (a) recover and reuse as much material as possible; (b) treat waste streams separately for getting better separation and recovery results; (c) utilize a range of waste treatment technologies for reaching the goal of waste minimization.

The objective of the present waste minimization study for the printed circuit board industry is to identify waste minimization technologies available to the industry, to develop engineering simulations for an in-process material recovering and recycling strategy, and to demonstrate the feasibility of an integrated waste minimization scheme for small and large PC board manufacturers. Since more than 60% (by weight) of waste from PC board production line results in aqueous, acidic, and alkaline solutions with metals [3], therefore, the reductions of these solutions are the major concerns of the present study. Two examples of waste minimization have been examined. Economic analyses of these two examples have also been conducted.

### SOLID/LIQUID SEPARATION ANALYSIS

In this section, several available experimental results for treating plating-related waste streams with different solid/liquid separation technologies, such as precipitation, reverse os available experimental data [18-27], we can determine the advantages and limitations of certain separation technologies. This information can provide basic knowledge for choosing suitable solid/liquid separation techniques to treat waste streams from the PC board manufacturing process, since there are very few experimental results available for this industry.

**Precipitation:** Nearly 75% of the plating facilities employ precipitation as the treatment scheme for removing metals from solution [6, 18]. From our review of fifteen waste treatment case studies for printed circuit board manufacture, we also find that more than 50% of manufacturers adapted the conventional sludge system to treat their waste streams [1-3, 8, 17]. There are three major precipitation methods widely used in industries, such as hydroxide or lime precipitation, sulfide precipitation, and sodium borohydride precipitation.

The traditional hydroxide precipitation method, due to ease of automatic control, is well proven and accepted in industry. However, there are several limitations of this method, e.g., the removal of metals of mixed metal wastes may not be effective because the minimum solubilities of different metals occur at different pH conditions [19]; the presence of chelating agents have an adverse effect on metal removal [18]; sludge quantities can be substantial and are generally difficult to dewater due to the amorphous particle structure; and little metal precipitation occurs for pH < 6.

An alternative to hydroxide precipitation involves sulfide precipitation [19]. This is very effective process for removal of metals due to the low solubilities of metal sulfides. There are several advantages of sulfide precipitation over hydroxide precipitation: for example, low retention time requirements in the reactor due to the high reactivities of sulfides; attainment of a high degree of metal removal even at low pH  $(2 \sim 3)$ ; metal sulfide precipitation is less influenced by the presence of complexes and chelating agents than the corresponding metal hydroxide precipitation, etc. [18]. The disadvantages of sulfide precipitation are the potential H<sub>2</sub>S gas evolution and the toxicity of sulfide.

Sodium borohydride precipitation can also be substituted for hydroxide precipitation to achieve lower effluent concentrations. Sodium borohydride is a strong reducing agent, capable of precipitating many metals in their elemental form [6]. This reaction is dependent upon the following process conditions and operational parameters: pH, temperature, metal concentration, the kinetics of competing reactions, agitation, residence time, and the method of solid/liquid separation. Compared with conventional treatment, this process offers the additional advantage of producing a low volume of sludge. A drawback is the high cost of the sodium borohydride reagent.

Ion Exchange: From the review of fifteen case studies [1-3, 8, 17] of the waste treatment of printed circuit board manufacture, we notice that there has been interest in using ion exchange (IX) to recover metals from waste streams. However, very few ion exchange experimental studies have discussed the operating conditions, limitations, the characteristics of resins, the efficiency of regeneration, and the recovery of the spent regenerant solution for treating different waste streams from PC board manufacturing processes.

There are several advantages of using ion exchange technique to treat metal-containing solutions [21]: e.g., IX is not adversely affected by the dilution of the solution being fed to the unit; rinsing with relatively high flow rates can be used effectively; a high capture efficiency is typical (metal discharge can be less than 1 mg/L); the energy cost is low; product concentration is higher than that of reverse osmosis, etc..

One study [21] has shown the experimental results of chelating ion exchange to treat printed circuit board wastes containing complexed copper from alkaline rinse dumps, electroless copper dumps, and different rinse effluents. The experiments run through a 24-in.-deep (61 cm) resin column at 1 gal/min/ ft<sup>3</sup> (133.7 L/min/m<sup>3</sup>). The copper concentration in the mixture ranges from 2 to 65 mg/L. The results show that the higher the copper concentration of the influent, the poorer the separation. They also found that as the flow rate increases, an early breakthrough of copper from the column is observed.

Gold *et al.* [20] conducted a series of experiments to treat the contaminated electroless and electrolytic nickel plating baths with different chelate resins. For treating the electroless nickel bath, their results show that the Amberlite IRC-718 resin is more selective to copper (94%) than nickel and is relatively selective to zinc and lead (50%). However, the removal of iron and chromium (+6) is even more difficult. With Duolite ES-467 resin, the resin shows excellent lead and zinc removal (89%). The copper removal is about 75%, however, the copper leakage is about 40% at the end of run. Only a small amount (5%) of chromium (+6) is extracted.

The experiments for treating the electrolytic nickel plating bath shows that with IRC-718 resin, the removal of copper and iron is superior to that of chromium (+ 6), lead, cadmium, and zinc. The least efficient removal (10%) is nickel; however, the leakage of lead and zinc exceeded 85%. A higher selectivity for the contaminated metals is observed relative to nickel for ES-467 as compared to IRC-718 resin. Lead and iron are almost completely removed; over 85% of cadmium and 25% of nickel are extracted. Gold *et al.* also suggested that a more suitable treatment would be removal by IRC-718 followed by ES-467. They predicted that with this arrangement, 90% of copper, iron, chromium (+ 3), and lead, and 75% of cadmium and zinc may be removed. However, about 33% of nickel would also be extracted.

Regenerating the saturated resin and recovering the spent regenerant solution are also important for using ion exchange technology to separate metal from waste streams. Etzel et al. [22] have conducted a series of experiments to investigate the application of the chelating agents for regenerating a strong cation exchange resin. Their study shows that the sodium form of EDTA (ethylenediamine tetracetic acid), NTA (nitrilotriacetic acid), or CIT (citric acid) can be used to regenerate a strong cation exchanger that has been exhausted with copper, zinc, and nickel. It is found that almost complete regeneration can be obtained between pH 6 and 9. Their results also show that regeneration effectiveness for a copper, zinc, and nickel exhausted exchanger with EDTA, NTA, and CIT is in the order copper > zinc > nickel. Regeneration effectiveness of EDTA, NTA, and CIT varies as the number of sodium ions available for exchange per mole of chelating agent solution. On this basis EDTA and CIT are better than NTA.

Etzel et al. [22] also find that an electrodialysis method (with a cation transfer membrane made of cross-linked sulfonated copolymer of vinyl compound) is efficient to recover metal and chelating agent from spent regenerant solutions. About 97 percent of recovery of EDTA and copper have been observed. The strong cation resin was exhausted with copper, regenerated with EDTA, and the EDTA-copper solution was recovered by an electrodialysis unit; for five cycles, no additional EDTA was required. The economic analysis also showed promise for this regeneration, recovery, and reuse process.

Although IX is an attractive method for removing metal ions from waste streams, considerable capital is usually involved. Cost reductions are dependent upon developing the ability to process water more rapidly. For both speeding up the regeneration and wastewater processing rates, Eco-Tec Corporation of Canada has developed a thin circular ion exchange bed of fine mesh beads (~100 mesh). One case study [17] shows that with the Eco-Tec short-bed, reciprocating-flow ion exchange unit, the copper-containing wastewater flow rate can be as high as 20 gal/min/ft<sup>3</sup> (2,674 L/min/m<sup>3</sup>), which is not greatly higher than that (1-15 gal/min/ft<sup>3</sup>, i.e., 133.7-2,006 L/min/m<sup>3</sup>) of the conventional resin system (20-50 mesh). However, the regeneration time can be as short as 4 minutes (the regeneration time of a typical conventional ion exchange unit is about 2 hours).

Grinstead and Paalman [34] also conducted a series of experiments with fine mesh resins (200-600 mesh), and thin bed (3-9 mm) supported on a microfiltration membrane (3 micron pore diameter). This system was used to process wastewater containing NaCl as well as Cu, Ni, Pb, Zn, and Cr (+3) ions. For efficient separation (90% metal ion removal ratio), the important conclusions are (1) for 200-325 mesh resin, the volume flow rate can be as high as 150 gal/min/ft<sup>3</sup> (2.00 × 10<sup>4</sup> L/min/m<sup>3</sup>), and (2) for 325-600 mesh resin, the volume flow rate is as high as 450 gal/min/ft<sup>3</sup> (6.02 × 10<sup>4</sup> L/min/m<sup>3</sup>). Flows can be very high, leading to relatively shorter cycle time.

Reverse Osmosis: Reverse osmosis is readily adaptable to the recovery of plating chemicals and water and is a continuous, low-energy process with simple operations. Three types of RO membrane configurations are used in commercially available units: tubular, spiral wound, and hollow fiber. Three types of semipermeable membrane materials can be used in RO units: cellulose acetates, hollow fiber polyamides, and polyether/ amide on polysolfone membranes (thin film composites). The cellulose acetate membranes have a narrow pH range which varies from 2.5 to 7 [7]. The allowable pH range (4 to 11) for hollow fiber membranes is broader than that for cellulose acetate [6, 7]. The membranes of new thin-film composites have received more attention recently [26]. This type membrane shows better pH stability in a wide range of pH  $(2 \sim 11)$ , and also withstands higher operating temperature than other kinds of membranes.

One experimental study [23] has investigated the treatability of acidic copper plating solution with two different kinds of membranes: one is the ultrathin cellulose acetate membrane (Eastman 398-10), and another is a special designed membrane NS-1 (microporous polysulfone support film coated with polyethylenimine). The experimental results show that the NS-1 membrane exhibited a constant copper rejection at 99.8% with only a small decrease in water flux during the test. For the Eastman 398-10 membrane after 210 hours of testing the copper rejection had decreased significantly with a corresponding increase in water flux; hydrolysis of the cellulose acetate membranes accounted for the decrease.

Werschulz [27] indicates that several reverse osmosis systems with polyamide, cellulose acetate, and thin-film composite membranes have been installed to recover copper sulfate from waste streams. He also sees applications of reverse osmosis to tin/lead plating solution and rinse water. However, very few experimental results discussed the application of reverse osmosis systems to treat the wastewater and spent solution from the electroless copper plating line.

Holland *et al.* [28] have shown one example of reverse osmosis technology to recover and recycle copper cyanide from the contaminated rinse water of a copper cyanide plating line. The system was a two-stage rinsing/recycling process achieving 98% of rejection of copper cyanide. The recovered copper cyanide solution and rinse water can be directly reused.

#### Summary

From the above review of several solid/liquid separation experimental results, we find that

- (1) the chelating agents in the metal-containing solution may influence the separation performance;
- (2) several kinds of separation technology may not be effective for the removal of metal in mixed metal wastes;
- (3) pH control is important for obtaining effective sepa-



Electroplating Line

FIGURE 1. Example Floor Plan for a Small Manufacturer with Two-Stage Rinsing/Recycling System.

Chemical	Monthly Usage	Cost Per Month
Ferrous Sulfate	850 lbs (386 kgs)	\$ 280~300
Alum	850 lbs (386 kgs)	\$ 400~500
Sodium Hydroxide	200 gal (0.76 m <sup>3</sup> )	\$ 180~200
Polyelectrolyte	1.4 kgs (3 lbs)	\$ 30~ 50
Sludge Disposal*	200-300 gal (0.8-1.1 m <sup>3</sup> )	\$ 300~400
	Т	otal \$1.200~1.450

ration with every separation technology (ion exchange or reverse osmosis technology);

- (4) reducing the quantity of sludge is important for printed circuit board waste treatment;
- (5) although ion exchange is an efficient separation scheme, the resin selection, regeneration of saturated resin, process control for avoiding breakthrough, and reuse of regenerant should be considered;
- (6) reverse osmosis with new membrane technology has the potential to be an efficient separation scheme for recovery and reuse of chemicals;
- (7) the recovered solution from any separation unit may be further treated in a solution tank for better quality and concentration control before transferring back to the process bath.

From the above summary, we also find that (a) the waste streams of the electroless copper plating line must be segregated since they contain chelating agents; (b) ion exchange or reverse osmosis technology can be used to treat the waste streams of electroplating lines (such as copper, tin/lead, or nickel/gold platings); (c) the proposed multi-stage counter-current rinse system [35] can be used to reduce the water usage and the wastewater generation rate, and thus reduce the sludge quantity; and (d) for avoiding the difficulties of treating the mixed metals solution, segregation of the waste streams is crucial.

In the following sections, two examples of the integrated waste minimization scheme are presented; one is for a small manufacturer and another is for large manufacturers. The waste stream segregation, in-process recovery and recycling, and automated continuous processing are demonstrated.

### WASTE MINIMIZATION FOR A SMALL PRINTED CIRCUIT BOARD MANUFACTURE WITH SEPARATION/RECYCLING RINSE SYSTEMS

Figure 1 shows a floor plan of a small printed circuit board manufacturing process. This process is generally divided into four categories: board and surface preparation, electroless plating, electroplating, and etching [J]. Nine dip-rinse and three spray-rinse operations are used; most are single-stage rinse units. The production rate is about 3,000 to 4,000 ft<sup>2</sup> board/month (279 to 372 m<sup>2</sup> board/month), and approximately 10<sup>4</sup> gal/day (37.8 m<sup>3</sup>/day) waste rinse water are generated [J].

### **Conventional Treatment**

The waste rinse water is treated at the industrial waste treatment plant with the conventional sludge treatment method. The treated water is then discharged to a water pollution control plant, where the maximum allowable concentrations of metals [1] in the discharged effluent are as follows: Chromium: 1.0 mg/L; Copper: 2.7 mg/L; Lead: 0.4 mg/L; Cyanide: 1.0 mg/L; Nickel: 2.6 mg/L; Silver: 0.7 mg/L; and Zinc: 2.6 mg/ L. The treatment chemicals and costs per month are listed in Table 2. The treatment generates about 2,400 gallons/year (9.08 m<sup>3</sup>/year) sludge containing different metals and solids. The sludge is landfilled as hazardous waste. In 1987, about \$2,000 to 3,000 was spent for sludge landfill. The total cost for wastewater treatment is about \$18,000/year or higher.

## The Multi-Stage Closed-loop Separation/Recycling Rinse System

In Figure 1, we have shown a suggested modification (dashed arrows) of the process for reducing water usage and waste water generation rate. The two-stage counter-current closedloop rinsing/recycling system, discussed in [35], is considered as an alternative of the present arrangement of the rinse systems. The three-stage closed-loop separation/recycling rinse system can also be applied; however, it may greatly increase the capital cost for equipment modification.

For the electroless copper line, a two-stage rinsing/recycling unit may be installed. A cation exchange unit may be used to treat the rinse effluent. The saturated resin can be regenerated by a chelating agent, e.g., EDTA. The spent regenerant solution, which contains EDTA-copper complexes, may be treated by an electrodialysis unit to recover EDTA [22]. The EDTA and water can be reused and the copper can be reclaimed. For the etchback/oxide line, one two-stage rinse system may replace the original single-stage rinse system. For the electroplating line, two sets of two-stage rinsing/recycling units (with either ion exchange units or reverse osmosis units or the combination of both) may be used for both copper and tin/ lead platings. Originally, boards removed from the etching bath are also rinsed in the rinse system of the electroplating line. Here, we suggest that another two-stage rinse system may be installed for better rinsing effect and for recovering rinse water and materials separately.

In Figure 1, we also show that for the electroless copper line and the etchback/oxide line, two rinse streams can be reused for the next rinse units. For example, in the electroless copper line, the rinse water for rinsing boards removed from the catalyst bath can be reused for rinsing boards removed from the accelerator bath. Several waste rinse streams (see process unit marked \* in Figure 1) may be treated by an independent separation unit (e.g., an ion exchanger or electrolytic cell). The treated water can be reused and the deposited copper reclaimed.

The Total Cost for the Modified Process: In our modified manufacturing process (Figure 1), three two-stage countercurrent separation/recycling rinse systems will be considered. Three single-stage rinse systems will be replaced with three two-stage rinse systems. One separation unit for treating mixed wastewater from different operating lines will also be installed. The total capital cost of this new process is about \$150,000 (four separation units will be installed, prices for different separation units are listed in Table 3 [1]) and the total operating and maintenance fee is about \$30,000 per year [6–8]. Extra rinse tanks (six of them) are needed (\$350/tank). The manufacturer may save \$20,000 to \$25,000/year from wastewater treatment and sludge disposal (see Table 2). With the conventional precipitation method, the capital cost of building a wastewater treatment plant (with 10<sup>4</sup> gal/day (37.8 m<sup>3</sup>/day)

Table 3 Comparison of Alternative Recovery Systems				
	<b>Reverse Osmosis</b>	Ion Exchange	Evaporation	Electrolytic Cell
Feed Conc.	Low	Very Low	High	Medium
Energy Required	Medium	Low	High	Low
Product Conc.	Low	Medium	Very High	Medium
Extra Chemicals	No	Yes	No	No
Replacement Time	$1 \sim 5$ years	~4 years		
Capital Cost	~\$30,000	\$38,000	\$45,000	~\$30,000
Capacity, gal/hr	100	20	20	15
(m <sup>3</sup> /hr)	(0.38)	(0.08)	(0.08)	(0.06)

water treatment capacity) is in the range of 50,000 to 75,000 [1, 3].

Chemical Recovery with the Modified Process: When the board production rate is around 3,000 to 4,000 ft<sup>2</sup>/month (279 to 372 m<sup>2</sup>/month), the plating solution density is 1.0 to 1.5 g/ml, for an average plating time of 100 hours/month plating time (i.e., five hours/day). The drag-out volume flow rate is 10 to 15 ml/ft<sup>2</sup> board (108 to 161 ml/m<sup>2</sup>); thus from our previous study [35], we find the drag-out rate from the plating bath is 1000 g/hr, and the recovered solution flow rate varies from 400 to 800 g/hr. We also find that the metal weight fraction in the recovered solution ranges from 0.37 to 0.59 as the metal weight fraction in the drag-out from the plating bath is 0.29 [35]. Therefore, about 150 to 480 g/hr of metal can be recovered, i.e., 20 to 50 kg/month. The unit price of copper or copper sulfate ranges from \$2.2/kg to \$11/lkg [6, 33]. If the price of the recovered tin/lead is similar to that of copper, the manufacturer may save \$1,300 to \$13,000/year for both electroplating and electroless lines. This estimation provides values similar to those given by previous studies [6, 7] (about \$2,000 to \$15,000/year savings for recovering different chemicals).

### Water Usage Reduction and Process Comparison

With the suggested two-stage closed-loop separation/recycling scheme, the water usage can be greatly reduced. If the manufacturer applies proper drag-out control and suitable operation of the separation units, the rinsing rate of every rinse system can be as low as 10 gal/hr ( $0.038 \text{ m}^3/\text{h}$ ). If the manufacturer cleans the rinse tanks (with 100 gal/tank or  $0.38 \text{ m}^3/$ tank capacity) twice a month, then water usage of this suggested closed-loop rinsing system will be about 4,000 gal/month (15.1 m<sup>3</sup>/month). This is based on a total of 16 tanks and the assumption that about 1% make-up water must be added to each rinse system because some water is lost from the separation unit. The water lost is much lower (98% lower) than that  $(10^4 \text{ gal/day or } 37.8 \text{ m}^3/\text{day})$  of the original (open-loop) rinsing system.

Comparing these two waste treatment schemes, conventional-sludge and multi-stage closed-loop rinsing/recycling, we find that although the capital cost of the latter is higher than that of the former ( $\sim$  \$80,000), the latter scheme can save water treatment chemical costs and process material costs of  $\sim$  \$25,000/year. Therefore, it is possible for the manufacturer to gain net benefit from the investment of four separation units for this multi-stage closed-loop rinsing/recycling scheme within four years if the operating and maintenance costs of both schemes are similar (tax and interest rates are not included). Table 4 shows the comparison of these two treatment schemes.

### COMPARISON OF THE ZERO-SLUDGE AND IN-TEGRATED WASTE MINIMIZATION SCHEMES FOR LARGE MANUFACTURERS: A FEASIBILITY STUDY

For large printed circuit board manufacturers, the processes are more complicated than those of small manufacturers. More than 50 operation steps may be involved in the entire process, and a huge amount of rinse water is used. The waste composition in the waste streams is complex [3], and there are several different approaches to treat the waste streams [3, 8, 17]. The two zero-sludge treatment schemes [3, 8] and our integrated waste minimization scheme for large manufacturers will be discussed and compared below.

### The Zero-Sludge Schemes

Higgins [8] proposed a waste minimization process for a

## Table 4 The Preliminary Cost Comparison For The Conventional Sludge Scheme And The Integrated Waste Minimization Scheme

	Conventional	Closed-loop Two-stage
	Sludge System [1, 3]	Rinsing/Recycling System
	(\$,000)	(\$,000)
Total Capital Cost	50~75	~150 (4 units)
(including installation		(a unit includes prefilters, pump,
labor charge)		adsorption column, pipings, etc.)
Annual Operating/Maintenance Fee	~ 40	35~45
(including module, filter replacement,		
and electricity costs (\$0.05/kw.hr))		
Annual Chemical Recovery Savings	0	2~13
Annual Chemicals Cost	20~25	~3
(including water usage	(water usage is	(water usage is
(\$0.9/10 <sup>3</sup> gal or \$0.9/3.78 m <sup>3</sup> ),	about $2.0 \times 10^6$ gal	about $5.0 \times 10^4$ gal
chemicals, and waste disposal)	or 7,500 m <sup>3</sup> )	or 189 m <sup>3</sup> )



FIGURE 2. Mixed-Stream Waste Treatment Scheme with Electrolytic Cell, Ion Exchange, Filtration, and Adsorption Techniques.

large PC board manufacturer. To minimize hazardous waste, the manufacturer treats the mixed waste rinse water by chelating ion exchange. It is found that chelating ion exchange resins adequately remove copper from the complexing agents, and allow the complexing agents to pass through to the effluent. Resins are then regenerated to produce a mixture of sulfuric acid and copper sulfate, which is then treated in an electrolytic cell to recover copper. Instead of recycling the treated rinse water, it is discharged to a publicly owned treatment facility. Since the total existing rinse flow rate is large, i.e., 50 to 90 gal/min (0.19–0.34  $m^3/min$ ), the total capital cost of this system (including filters, pumps, tanks, mixers, and installation) is higher than \$650,000 and the annual op-



FIGURE 3. Semi-Segregated Waste Treatment Scheme with Electrolytic Cell, Ion Exchange, Filtration, and Evaporating Units.

erating cost is about \$150,000. The flow diagram of this waste treatment system is shown in Figure 2.

The study [3] also proposed a general mixed-stream waste treatment system (a zero-sludge system) for printed circuit board manufacturers. Mixed dilute metal-containing rinse water is treated by ion exchange, while spent solutions, etchants, spills, etc., are treated by an electrolytic cell. The regenerated solution from the ion-exchange columns is also treated by the electrolytic cell. The treated stream after leaving the ion exchanger may be either discharged or further treated by a demineralization unit and the resulting de-ionized water can be reused. The recovered metal from the electrolytic cell may be reused or sold. The developer and stripper solutions are first treated by a solid separation unit and then by an evaporation system. The resulting sludge is then sent for off-site disposal. The economic analysis of this system for a large manufacturer with 3,000 ft<sup>2</sup> board/day (279 m<sup>2</sup>/day) production rate and 10<sup>5</sup> gal/day (378 m<sup>3</sup>/day) water usage shows that the capital and annual operating costs are \$1,000,000 and \$179,000, respectively. The flow diagram of this waste treatment system is shown in Figure 3.

Next we propose an example of integrated waste minimization to reduce waste production for a large printed circuit board manufacturer. Integrated waste minimization is a comprehensive approach to waste reduction that utilizes new processes, methodologies, and treatment methods integrated into the manufacturing process. Waste minimization is accomplished by in-process recycling, and resource recovery, assisted by process automation. In this example, the production of metal-containing wastewater or solution is minimized by recycling the concentrated metal-containing solution and reusing the rinse water.

### The Integrated Waste Minimization Scheme

For large-scale PC board manufacture (see the flow diagram in Figures 4 to 6 [3, 15, 16]), an integrated waste minimization scheme for the electroless copper line, electroplating line, and etching and stripping line will be discussed. The tin-lead fusing, etchback, smear removal, and gold-nickel plating steps will not be considered here.

### The Electroless Copper Line

There are three variations of the integrated waste minimization scheme for the electroless copper line (see Figures 4.a to 4.c). An automated micro-etch (with sulfuric acid and hydrogen peroxide solution) system is used for all of these three variations. The system consists of an etching unit, crystallization (for recovering and recycling copper sulfate) and replenishing units, and a separation unit (consisting of an ion exchange column and an electrodialysis system), which will treat the wastewater from the rinse system after the electroless copper plating and neutralization baths.

(1) The first variation is shown in Figure 4.a. The wastewater effluents from three different rinse systems (after the cleaner-conditioner, micro-etch, and catalyst steps) are treated with a centralized separation unit. The purified water will be recycled back to each rinse system. The metal-containing residue or effluent from the separation unit may need further treatment. A small amount of fresh make-up water may be necessary for each rinse system to compensate the water loss from the separator.

(2) If the used rinse water from the rinse system after the cleaner-conditioner bath is reused in the next rinse system after the micro-etch bath (see Figure 4.b), then the water usage can be greatly reduced. The used rinse water may flow into the last stage and the fresh make-up water with the recycled rinse water (from the separator) will be input into the first stage of



FIGURE 4a. Integrated Waste Minimization Process with Wastewater/Etchant Recycling Units for Electroless Copper Line.



FIGURE 4b. Integrated Waste Minimization Process with Wastewater/Etchant Recycling Units for Electroless Copper Line.



FIGURE 4c. Integrated Waste Minimization Process with Wastewater/Etchant Recycling Units for Electroless Copper Line.

the multistage rinse system. The first rinse system is mildly alkaline because the cleaner is an alkaline solution. Since the micro-etch drag-out is acidic, transferring the used rinse water from the first rinse system to the rinse unit after the microetch process will neutralize the rinse effluent before flowing into the separator. This approach will reduce both the capital cost (because the size of the separator will be small) and the operating/maintenance fee (pH adjustment cost) of the separator.

(3) The third variation is shown in Figure 4.c. The difference between Figures 4.b and 4.c is that an independent separation unit with solvent extraction process [9], used to treat the effluent from the rinse system after the catalyst bath, is installed to recover and recycle catalyst (PdCl<sub>2</sub>) from wastewater. Obviously, this approach will increase the capital cost for an extra separator (cost is unknown), but the purchasing cost of catalyst may be reduced. This will also further reduce the amount of metal-containing residue or sludge generated by the process of Figure 4.a or 4.b. For recovery of precious palladium catalyst, the recovery cost varies with the metal contents in the waste because the refining process includes analyzing, preparation, and processing steps. The analysis [32] indicates that pre-enrichment is necessary to make the recovery profitable. Brumy [32] has demonstrated that the recovery cost of palladium catalyst is about \$6,000/Kg for palladium content varying from 0.043% to 0.09% in the waste. The cost of virgin PdCl<sub>2</sub> is about \$7,500/Kg [33].

### The Electoplating Line

For the electroplating line, we consider the following steps: image transfer (coat with resist material and develop resist), micro-etch, acid dip, and copper and tin/lead plating. The major wastes of this electroplating line include spent acid, spent developers/cleaners (caustic soda or 1,1,1-trichloroethane, and freon), spent etchants, spent plating solutions, and wastewater; all contain metal ions or salt and some organic chemicals.



FIGURE 5a. Integrated Waste Minimization Process with Wastewater Separation/Recycling Unit for Plating Line.

(1) Image Transfer Process Variations: There are two basic image-transfer processes, screen printing and photoprinting. For the dry-film photoprinting process, if the solvent-based developing technique is applied for image-transfer, the spent developers (freon and 1,1,1-trichloroethane) can be recovered by an evaporation and distillation system. A flash evaporator can be used to recover spent 1,1,1-trichloroethane. The freon can be recovered from the spent developer bath by a distillation



Proceed to Etching/Stripping Line

FIGURE 5b. Integrated Waste Minimization Process with Solution Recycling Unit and Continuous Plating System column. The purified chemicals can be reused; however, the still bottom of the distillation column, which contains high concentration of organic chemicals, such as resist monomers and chloronated chemicals, may need further treatment.

If the aqueous developing technique is adopted, the spent developer (potassium or sodium carbonate) solution may be treated with the spent acid (HCl or  $H_2SO_4$ ) from other steps to adjust pH. After settling and filtering out the flocculated resist, the solution can be neutralized and discharged.

Comparing the solvent-based and the aqueous resist developing (dry-film) techniques, the latter generates less hazardous waste (e.g. chloronated organic chemicals) than the former. Therefore, for reducing hazardous waste generation, it is more suitable to apply the latter technique than the former one. Furthermore, the chemical cost and waste treatment cost of the aqueous developing technique are also low; however, the quality control may be difficult. This may be overcome by using an automated continuous replenishing (potassium or sodium carbonate) system [5] with a pH monitoring and control unit. This approach can reduce the amount of replenishing solution and wastewater generation up to 25% [5].

Besides the dry film photoresist image-transfer technologies, the screen-printing process is also a major technique for imagetransfer [31]. For the screen-printing process, the screen fabrication, preparation, and ink characterization are important. The ink should be alkaline-strippable and thermal-, UV-, or air-cured. Since no other solvent-developing step is needed for the screen-printing process, the environmental impact of this technique is low. The pollution sources of the screen-printing process are used ink and spent screens, which need off-site treatment.

(2) Spent Acid Treatment: The spent acid  $(H_2SO_4)$  may be treated in two different ways: (a) neutralized with alkaline solution from other steps of the manufacturing process, followed by a precipitation and settling unit, and (b) purified with an acid purification unit and then transferred back to the bath for reuse. The rinse water effluent from the rinse system (see Figure 5.a) following the micro-etch unit. This may reduce water usage greatly.

(3) Rinse Water Reuse and Recycling: The waste rinse water and spent plating solution can be treated with the continuous plating and closed-loop multi-stage separation/recycling rinse system. The purified rinse water can be reused and the recovered solution, after further treatment (see below), can be transferred to the solution tank for reusing. For the microetch step, an automated system can also be applied (similar to the one discussed in the electroless copper line) to reduce the waste generation and to recycle materials. Figure 5.a shows the flow diagrams of the electroplating process with the inprocess recovery and recycling systems.

The continuous plating and closed-loop rinsing/recycling system (see Figure 5.b) consists of (a) a separation unit to treat the waste rinse water, (b) a multi-stage closed-loop rinsing system for reducing the water usage and wastewater generation, (c) a carbon adsorption and filtration system, (d) an evaporator to concentrate the recovered solution, and (e) a solution tank to store the treated solution and then mix with the virgin solution for reuse. The carbon adsorption and filtration system treats the recovered solution from the separation unit and the overflow solution from the plating bath for reducing the organic and particulate contaminants (this is important for the copper plating bath because it follows the micro-etch and the image transfer steps). The full continuous plating and closedloop rinsing/recycling system is needed for copper plating; however, for tin/lead plating, the adsorption and filtration system may not be necessary.

### The Etching and Stripping Line

The etching and stripping line includes the following steps:



FIGURE 6. Integrated Waste Minimization for Etching/ Stripping Line.

acid dip (optional), rinse, neutralization, micro-etch (optional), alkaline etch, and stripping. Many chemicals, such as hydrochloric acid, sulfuric acid, ammonium etching solution, potassium hydroxide (or methylene chloride) stripper, etc., are used. The flow diagram of the etching and stripping line is shown in Figure 6.

The used rinse waters of the first rinse system and of the rinse after the sulfuric acid dip may be reused for the rinse after the micro-etch unit and for the rinse after the ammonium

W

etch bath, respectively. This will reduce the water usage significantly. Multi-stage rinse units will be adopted for each rinse system. This will further reduce the water usage. A centralized separation unit will be installed to treat all wastewater from every rinse system except the last one after the stripping bath. The treated rinse water can be reused and the residue (metal or metal salt) can be reclaimed. The wastewater from the last rinse system contains stripped resists, which can be removed by gravitation and filtration methods. After treatment, the rinse water can be reused.

Alkaline ammonia etching with ammonium hydroxide and chloride is increasingly used because of its continuous operation, fast etch rate, etc. [30]. The automated closed-loop etching, replenishing, and rinsing system is available for better quality and pollution controls. The copper-containing rinse water must be treated by a separation unit and recycled. The spent etchant and the spent stripper (KOH) may be neutralized by spent acids and then discharged. An acid purification unit can be used to purify and reuse the spent acids, or the spent acids can be neutralized and discharged.

### Water Usage Reduction

With the integrated waste minimization scheme, the water usage can be reduced significantly. Since a three-stage closedloop separation/recycling rinse system is applied in this example, totally about 39 rinse tanks (100 gal or 0.38 m<sup>3</sup> for each) are installed for electroless copper, electroplating, and etching/stripping lines. If the operator cleans tanks twice a month and if 1% (in volume) make-up water is added to each rinse system (13 systems) in the process, then less than 10<sup>4</sup> gal/month (37.8 m<sup>3</sup>/month) of water will be used. The total water usage in a year will be less than 1% of the original water usage, i.e.,  $2.5 \times 10^7$  gal/year or  $9.46 \times 10^4$  m<sup>3</sup>/year (see Table 5).

### **Economic** Analysis

This integrated waste minimization system, Figures 4.a to 4.c, includes five three-stage counter-current rinsing/recycling

Table 5 Cost Compar	ison* For "Zero-Sludge'	' and Integrated Waste M	Ainimization Schemes
large printed circuit board manufa /astewater: 10 <sup>5</sup> gal/day or 378 m <sup>3</sup> /c	cturer: Production Rate: - lay (originally); working: 2	-4,000 ft <sup>2</sup> ( $-372$ m <sup>2</sup> ) board 50 days/year (2 shift)	l/day;
	"Zero-Sludge" Wast	e Treatment Schemes	Integrated Waste
	Process examined in Figure 2 [8] (\$,000)	Process proposed in Figure 3 [3] (\$,000)	Minimization Scheme proposed in Figures 4~6 (\$,000)
Capital Cost (tanks, IX, or ED, or EC, or EV, or RO, filters, and labor costs)	~ 650	~1,000 (5 units; including a control system)	~700** (7 or 8 units)
Annual Operating And Maintenance Cost (electricity, chemicals, resins, modules, residue disposal, water, etc.)	~ 150	170~180	140~150
Process Chemical Recovery Savings (per year)	0	0	~15-150
* <u>Annual Water Usage</u> , gallons (m <sup>3</sup> )	2.0×10 <sup>7</sup> (7.56×10 <sup>4</sup> )	$1.0 \times 10^7$ (3.78 × 10 <sup>4</sup> ) with water (partially) recycling system	$1.0 \times 10^{5}$ (378) with closed-loop three-stage rinsing/recycling systems

\* The capital and annual operating/maintenance costs of a conventional-sludge system for treating waste streams from a large manufacture are in the order of \$500,000 or higher and \$220,000, respectively [3].

\*\* We find that if the screen printing process or the aqueous dry-film developing process for image-transfer is used, then costs for recovering freon and 1,1,1trichloroethane (developers) can be saved. This will greatly reduce the total capital cost to less than \$400,000 (with 5 or 6 separation units) for the integrated waste minimization scheme. systems for the electroless copper line (with one ion exchanger and one electrodialysis system in Figure 4.a or 4.b), electroplating lines (e.g., copper and tin/lead plating lines with reverse osmosis or ion exchange or both, evaporator, adsorption, and filtration systems), one centralized mixed-stream wastewater separation and recycling unit to treat all other waste rinse water (with an evaporator or ion exchanger), and a distillation/evaporation system to recover spent developer and cleaning solutions (e.g., methyl chloroform or 1,1,1-trichloroethane, freon, and perchloroethylehe) [2]. An acid purification unit (ion exchanger) [29] may be installed to clean and recycle different used acids.

(1) The Total Cost for the Integrated Waste Minimization Scheme. The automated etching and replenishing process [30] for both micro-etch and ammonia etch steps is assumed to be a standard method to replace the original "batch" etching steps to improve the quality of PC boards and to reduce the usages of etchant and water. However, the cost of process is not included in the economics analysis. The total capital cost of the integrated waste minimization scheme may be in the order of \$700,000 for seven or eight separation units (see prices for different separation units in Table 3 and [2]). The annual operating and maintenance fee is of the order \$150,000 (including residue disposal, module or resin replacement, and electricity costs).

(2) Chemical Recovery. A continuous plating process (with a closed-loop rinsing/separation system) will allow the quality of the process solution to be well-controlled and also requires less frequent treatment of the spent solution. Furthermore, the recovered process solution and rinse water can be reused, and the manufacturer can reduce chemical purchasing and water usage costs.

The savings of chemical purchasing can be estimated for the following case: the board production rate for a large firm is about 3,000 to 4,000 ft<sup>2</sup>/day (279 to 372 m<sup>2</sup>/day), the plating solution density is between 1.0 to 1.5 g/ml, the plating time averages 200 hours/month (i.e., ten hours/day, two-shift), and the drag-out volume flow rate is 10 to 15 ml/ft<sup>2</sup> of board (108 to 161 ml/m<sup>2</sup>). Then from our previous calculation [35], we find that as the drag-out rate from the plating bath is about 8,000 g/hr, the recovered solution flow rate varies from 2,400 to 7,000 g/hr. We also find that the metal weight fraction in the recovered solution ranges from 0.3 to 0.9 as the metal weight fraction in the drag-out from the plating bath is 0.29 [35]. Therefore, about 700 to 6,300 g/hr of metal can be recovered, i.e., 140 to 1,200 kg/month. The unit prices of copper or copper sulfate range from \$2.2/kg to \$11/kg [6, 33]. If the price of the recovered tin/lead is similar to that of copper, the manufacturer may save \$15,000 to 150,000/year for both electroplating and electroless lines.

The economic analyses of four different waste treatment schemes, i.e., the conventional-sludge system [3], the two zerosludge systems [3, 8], and the integrated waste minimization process, are presented in Table 5. We find that the integrated waste scheme may be the most economic and efficient (although the cost for space modification is not included in this analysis).

### CONCLUSIONS

From the experimental data review, solid/liquid separation analysis, engineering calculations [35], and two example studies of waste minimization (Figures 1 to 6), we conclude the following:

(1) To reduce water usage and wastewater generation rates, recycling rinse water is an important waste minimization objective for the printed circuit board manufacturing process.

(2) Minimizing drag-out for both process bath and rinse tanks is important for waste minimization and material re-

covery in the printed circuit board industry. Drag-out control can be conducted by: (a) minimizing bath concentration by maintaining chemistry at the lower end of the operating range; (b) increasing the bath temperature can also reduce the viscosity and surface tension of the solution; and (c) withdrawing boards at slower rates and allowing sufficient solution drainage before rinsing, using drag-out tanks to recover process chemicals for reuse, etc.

(3) The multi-stage rinse system, because it reduces rinse water usage and substantially reduces the generation rate of wastewater, has advantages compared to the single-stage rinse system.

(4) An integrated waste minimization strategy can be applied to the printed circuit board manufacturing process. Two examples have been studied (see Figures 1 to 6). One can apply a multi-stage counter-current closed-loop rinse system with or without a separation unit, conduct careful drag-out control for each step, and reuse the lightly polluted rinse water from previous rinse tank for the next rinse system. If an automated continuous process is applied, it can give the manufacturer better quality control of the plating and teching solutions, and thus better treated boards. It also reduces costs for the regular spent solution unit for reusing or may be neutralized with an other alkaline solution and then discharged.

(5) The integrated waste minimization scheme also includes the alternative processing methods for generating less waste (without using freon and 1,1,1-trichloroethane). In our study, for example, we find that the solvent-based dry-film photoprinting process may be replaced with the less polluted aqueous dry-film developing or the screen printing process. (6) The total cost of the integrated waste minimization process is competitive with the conventional-sludge system and the zero-sludge systems.

(7) The best way required to treat waste streams from the PC board manufacturing process is to treat each waste stream separately and recover and reuse as much material as possible.

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# The Evaluation of Supplemental Oxygen Burner Firing in a Countercurrent Rotary Kiln

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Detailed tests were conducted to evaluate the process impact of treating contaminated soils by concurrently firing the Linde® Oxygen Combustion System (OCS) with the main kiln air-natural gas burner. The evaluation was carried out at the Louisiana Army Ammunition Plant (LAAP) on explosives-contaminated soil in International Technology's (IT) countercurrent kiln Hybrid Thermal Treatment System (HTTS<sup>®</sup>).

Cocurrent and countercurrent kiln firing positions (relative to soil flow) were utilized for the OCS at stoichiometric and substoichiometric oxygen ratios. The relative firing rates of the OCS and main burner were varied at a combined heat release of approximately  $8.8 \times 10^6$  W. A reference run was conducted to define process performance for the main kiln air-natural gas burner alone. The feed soil contained 18 to 22 ppm nitroexplosives at an average moisture content of 17.5 percent (dry weight basis). A constant ash discharge temperature of approximately 480°C was maintained during the basic tests.

The average heat transferred to the soil feed for the reference case was  $49 \times 10^3 W/m^2$  of kiln surface and for the OCS tests up to  $55 \times 10^3 W/m^2$  was transferred. The average heat release for the reference run and the OCS tests was  $160 \times 10^3 W/m^3$  and  $187 \times 10^3 W/m^3$  respectively.

Capacity increases of up to 20 percent were achieved by firing the OCS in a countercurrent mode at a substoichiometric oxygen ratio of 56 percent, resulting in an operating cost reduction of about 12 percent. Higher oxygen stoichiometric ratios did not produce proportionally increased throughput.

### INTRODUCTION

With increasing frequency, remedial investigation/feasibility studies (RI/FS) are recommending thermal treatment as the technology of choice for remediating contaminated pits, ponds, lagoons, and soils at Superfund, state and private sites. Thermal treatment of soil must meet specific ash quality criteria at competitive treatment costs. Unit treatment costs are inversely related to treatment capacity, which, in turn, is directly related to the heat transfer rate to the soil solids. To further optimize treatment capacity through increased heat transfer, supplemental oxygen combustion was evaluated for IT Corporation's (IT's) HTTS at the Louisiana Army Ammunition Plant (LAAP). This evaluation was carried out upon completion of the thermal remediation of more than 133,000 metric tons (mt) [147,000 tons (t)] of nitroexplosive-contaminated soils with IT's HTTS at LAAP. The tests were performed from March 28 to April 2, 1990 with approval of the U.S. Army, the



FIGURE 1. Typical parametric interrelationships for a countercurrent rotary kiln treating lightly contaminated soils

Louisiana Department of Environmental Quality (LDEQ), and the U.S. Environmental Protection Agency (EPA) Region VI.

Because the kiln was already at its thermal design capacity, supplemental oxygen combustion was selected as one option to evaluate for optimizing the HTTS kiln throughput per unit of energy input (mt/W or t/MM Btu). Therefore, any capacity increase would have to result from an improvement in heat transfer efficiency at the same thermal duty. The LINDE Oxygen Combustion System (OCS) provided by the Linde Division of Union Carbide Industrial Gases Inc., was selected for evaluation because of its potential to improve heat transfer via its unique flue gas recirculation characteristics. Recirculation increases the average temperature of the heat transfer zone and maintains a more uniform temperature within the zone.

A series of tests were conducted to evaluate the capacity and process impact of treating contaminated soils by concurrently firing the LINDE OCS in conjunction with the kiln main air burner. The evaluation focused on the HTTS countercurrent kiln because other downstream unit operations were not limiting system capacity or ash quality. Because the kiln was at thermal capacity, the total thermal input from both burners (main and OCS) was approximately equal to that fired by the existing main kiln air burner alone. The heat distribution between both burners was varied for each test, although the total energy input remained approximately the same. In performing this work, tests were initially conducted to develop a baseline reference point for the performance of the existing main kiln air burner alone. This served as a benchmark for measuring the impact of the OCS supplemental burner.

The OCS and baseline evaluations were conducted on explosives-contaminated soil containing 17 to 22 percent (dry basis) moisture and less than 20 parts per million (ppm) of total nitroexplosives. Cocurrent and countercurrent kiln firing positions (relative to soil flow) were utilized for the OCS at stoichiometric and substoichiometric oxygen ratios. The tests were conducted over a period of 9 days on a 24-hour-per-day basis without significant process interruptions.

### BACKGROUND

The program emphasis for increasing soil thermal treatment capacity and ash quality in the HTTS system focused on the countercurrent rotary kiln. Because the HTTS kiln was already operating at a high throughput [up to 19.95 mtph (22 tph)], maximum capacity increases with a supplemental oxygen burner were expected to be less than 20 percent. Although this level of increase would be economically significant, it was difficult to verify because of the multiple processing variables, time required to develop steady-state operation, and the large base

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capacity of the HTTS. The program was, in essence, a task of fine tuning a large-capacity kiln that had been previously optimized and operated at its thermal design capacity.

### **TECHNICAL APPROACH**

The thermal treatment of lightly contaminated soils containing 17 to 20 percent moisture (dry basis) requires almost equal amounts of energy to heat the dry soil residue to 482°C (900°F) and evaporate the moisture in the soil. However, basic energy balances alone do not address the kinetics of drying, desorption, or heat transfer that control the rate of soil treatment and ash quality in a kiln. Figure 1 is an empirical plot of the solids and gaseous temperature profiles and solids retention time along the kiln length. A study of the solids temperature and retention time curves indicate that at higher throughput capacities, well over half of the kiln length is utilized to heat the soil to the desired ash holding temperature. Consequently, the soil is generally at the optimal treatment temperature for only about 25 to 40 percent of its total retention time within the kiln at capacity throughput. The OCS tests were designed to measure any changes in soil treatment capacity per unit of energy input at the same outlet ash temperature. Ash temperature was the common basis used for comparing the results of all the test runs. Feed to the kiln was modulated until the ash temperature, as measured at the kiln outlet, stabilized at the target temperature for each specific test run.

The OCS was evaluated in two firing locations, at the kiln feed end and at the kiln discharge end. Heat transfer efficiencies and ash quality for each OCS burner location were directly compared to the baseline performance data obtained with only the existing kiln main air burner. All comparisons were based on approximately the same kiln ash exit temperature.

The purpose of evaluating the OCS burner at the kiln solids feed end was to determine if the larger temperature difference  $(\Delta t)$  between the OCS burner heat transfer zone and the ambient soil feed would enhance the overall heat transfer rate. Similarly, the OCS burner was located at the ash discharge end to improve the utilization of the heat transfer area at this end of the kiln. Figure 1 is helpful in explaining the strategy of evaluating the OCS burner at this location. Figure 1 indicates that a negative  $\Delta t$  may exist between the heated ash and the base (burner exhaust) of the main burner flame envelope. This could occur because the major release from the air-natural gas flame envelope takes place about 2 to 3 meters (7 to 10 feet) from the exhaust of the main burner. Consequently, the OCS burner was evaluated at this location to determine if this portion of the kiln could be utilized to accomplish a net positive transfer of heat to the ash. This OCS location could also increase the utilization of the overall kiln heat transfer area because the OCS combustion gases must traverse the entire length of the kiln before exiting into the hot duct.

Factors that could affect heat transfer efficiency and ash quality at each OCS burner location include the following:

- Emissivity of main burner flame envelope
- Length, shape, and location of the main kiln burner flame envelope
- Average temperature and temperature profile of the main kiln burner flame envelope
- Length, shape, and position of the OCS heat transfer zone
- Average temperature and temperature uniformity of the OCS heat transfer zone
- Average temperature of the heat sink
- · Emissivity of OCS heat transfer zone
- Emissivity of the heat sink
- Cocurrent or countercurrent firing relative to main air burner flue gas flow (This impacts the shape of the OCS burner recirculating zone.)
- Length of the kiln solid bed exposed to the flow of flue gases from the OCS burner (This includes the flue gas recirculation zone and resultant downstream plug flow.)





- Heat distribution between the OCS burner and the kiln main burner
- Stoichiometric ratio of pure oxygen to natural gas in the OCS burner
- Infiltration air and local flue gas turbulence at burner test locations.

Despite the large number of variables that could impact the performance results, the basic test structure was relatively simple. A significant technical challenge was to verify the actual performance changes from baseline conditions.

More than 2,721 mt (3,000 t) of soil were prepared in advance to ensure uniform feed moisture, particle size and size distribution, contaminant concentration, and handling characteristics. Instantaneous feed rate measurements were available from a continuous recording scale located on the soils mass flow feeder. However, the total soil processed for each test run was obtained by subtracting totalizer weight readings. Ash temperature were measured by two recording thermocouples located in the ash discharge duct. Critical flue gas flows and compositions were measured by the IT Air Quality Services group as well as by process monitors. Each run was approximately 9 hours in length, except for 4 runs that were approximately 4 to 5 hours in length.

### **PROCESS DESCRIPTION**

### **HTTS Incinerator**

The transportable HTTS has a rated thermal capacity of  $16.4 \times 10^6$  W (56 MMBtuh) with a high inert solids throughput capacity of up to 20 mtph (22 tph). Emissions and effluents from the system are treated, monitored, and controlled to levels well within permitted limits.

The system consists of three transportable core process modules—primary combustion, secondary combustion chamber (SCC), and air pollution control (APC) systems. A general block flow diagram of the equipment modules used at LAAP is shown in Figure 2. A cross section of the HTTS countercurrent kiln is shown in Figure 3. This figure identifies the processing zones that the soil solids pass through during their



### FIGURE 3. HTTS countercurrent rotary kiln for lightly contaminated soils operation





FIGURE 4. LINDE "A" Burner

travel through the kiln. Also shown are the relative positions of the existing kiln main air burner, the locations of the OCS burner, and the soil feed conveyor.

### **Oxygen Combustion System Burner**

The LINDE OCS includes the LINDE "A" (aspirating) Burner, oxygen flow control skid, natural gas flow control skid, and a local control console. Liquid (cryogenic) oxygen is stored under pressure and evaporated to a high pressure gas immediately before use. Figure 4 is a simplified schematic representation of the principles of operation of the LINDE "A" Burner. The pressurized oxygen gas is supplied to the multiple high velocity jets in the LINDE "A" Burner. Fuel is supplied at relatively low pressure. The furnace gases are aspirated into the high velocity oxygen jets before mixing with the central fuel jet. By maintaining sufficient distance from the oxygen jets and fuel supply, cooled furnace gases are aspirated into the oxygen mixing jet before fuel contact to reduce the burner flame temperature. In theory, the conventional air burner utilizes nitrogen as the diluent; for the LINDE "A" Burner, the recirculated furnace gases make up the diluent.

### **TEST RESULTS**

### **Baseline Test**

A baseline test (baseline 1) was conducted to document the performance of the HTTS with the kiln main air burner alone. This data base served as a benchmark for measuring the incremental capacity changes with the OCS burner at each position. Table 1 summarizes kiln and system performance over 9 hours of operation. Infiltration air and heat transfer values for all tests were calculated from heat and material balance results based on the test data. Steady-state capacity stabilized at 10.7 mtph (11.8 tph) of contaminated soil (20.6 percent moisture-dry weight basis) when  $8.3 \times 10^6$  W (28.3 MMBtuh) was fired in the kiln air burner. An average ash discharge temperature of 489°C (913°F) was maintained with a kiln exit gas temperature of 727°C (1340°F) over the 9-hour period. Stack gas flow was 331 dry meter<sup>3</sup> (dm<sup>3</sup>/minute (min) [11,674]

Table 1 Baseline 1 Test Results	
Parameter	Test Condition
Kiln heat release watts W (MMBtuh)	8.3×10 <sup>6</sup> (28.3)
Kiln feed rate mtph (tph)	10.7 (11.8)
Soil moisture content (% by dry weight)	20.6
Total nitroexplosives (ppm)	6.0
Total nitroexplosives in ash (ppm)	<1.3
Ash temperature °C (°F)	489 (913)
Kiln exit gas temperature °C (°F)	727 (1340)
Total combustion air to kiln burner dNm <sup>3</sup> /min (dscf/min)	163 (5,765)
Kiln infiltration air dNm <sup>3</sup> /min (dscf/min)	58 (2,046)
Stack gas flow dNm <sup>3</sup> /min (dscf/min)	331 (11,674)
Kiln shell heat loss W (MMBtuh)	$0.67 \times 10^{5}$ (2.3)
Heat transferred to feed W/m <sup>2</sup> (Btuh/ft <sup>2</sup> )	$4.3 \times 10^4 (1.35 \times 10^4)$
CO at stack (ppm corrected to $7\%$ O <sub>2</sub> )	0.96
$O_2$ at stack (% dv)	10.1
NO <sub>x</sub> at stack ( $ppm_{dy}$ corrected to 7% O <sub>2</sub> )	63

Notes:

The above values are average values for the baseline case during 9 hours of steady-state operations.

The average kiln rpm during the test was 1.54.

The kiln is a 2 m (6.5 ft) ID × 12 m (40 ft) effective length and has an internal refractory area of 75.9 m<sup>2</sup> (816 ft<sup>2</sup>).

Heat transferred to feed = [Heat required to evaporate moisture in soil at 100°C (212°F) + heat required to heat dry soil to 482°C (900°F) + kiln heat loss]/75.9 m<sup>2</sup> (816 ft<sup>2</sup>).

	Table 2a Su	ummary of M	(ey Operating	Conditions for Ba	seline and OCS Tes	sts at Feed Er	nd
						Kiln Burner	Firing Rate
Test Number	Solid Rate mtph (tph)	Moisture Content (% by dry weight)	Ash Temperature °C (°F)	Kiln Exit Gas Temperature °C (°F)	Kiln Infiltration Air dNm <sup>3</sup> /min (dscfm)	Oxygen Burner W×10 <sup>6</sup> (MM Btu/h)	Air Burner W×10 <sup>6</sup> (MM Btu/h)
<b>Baseline</b> 1	10.7 (11.8)	20.6	489 (913)	727 (1340)	58 (2,046)	0 (0)	8.3 (28.3)
1a	10.9 (12)	19.7	503 (937)	831 (1528)	59 (2,077)	1.2 (4)	8.1 (27.6)
2a	10.6 (11.7)	19.8	487 (908)	855 (1571)	69 (2,449)	2.2 (7.7)	6.9 (23.6)
3a	9.4 (10.4)	19.6	509 (949)	923 (1693)	88 (3,127)	4.1 (14.1)	5.0 (16.9)
Baseline 2	7.7 (8.5)	19.6	634 (1173)	773 (1423)	55 (1,936)	0 (0)	8.2 (27.9)
1b	10.0 (11)	19.3	603 (1118)	867 (1592)	48 (1,678)	1.1 (3.8)	8.3 (28.3)

dry standard cubic feet per minute (dscf/min)], which includes 163 dm<sup>3</sup>/min (5,765 dscf/min) and .58 dm<sup>3</sup>/min (2,046 dscf/min) of kiln combustion and infiltration air, respectively. The total heat transferred to the soil and lost through the kiln shell was  $3.25 \times 10^6$  W (11.04 MMBtuh) for an overall heat transfer efficiency of 39 percent or 0.42 tons of soil per each MMBtu fired. Kiln shell heat loss is included as heat transferred. The carbon monoxide and nitrogen oxide were at 0.96 and 63 parts per million dry volume (ppm<sub>dv</sub> corrected to 7 percent oxygen), respectively, in the stack gas.

An analysis of the baseline data indicates that of the total heat transferred from the main burner, 20.8 percent was dissipated as heat loss. If only one-half of this energy was captured, kiln capacity could theoretically be increased by more than 13 percent or approximately 1.45 mtph (1.6 tph). This level of heat loss is characteristic of many transportable systems that are constrained by size and weight limitations.

The baseline data also includes that infiltration air makes up 26.2 percent of the total air entering the kiln. The majority of this air appears to enter at the feed end around the feed belt and short circuits directly to the kiln outlet duct. Infiltration air was calculated by an oxygen balance around the kiln.

A separate baseline case (baseline 2) of 4 to 5 hours was conducted with the ash temperature targeted at  $593^{\circ}C(1100^{\circ}F)$  to develop a database applicable to contaminants requiring higher ash treatment temperatures. The data for this test are reported in Table 2a. The run time for this test may have been too short to achieve steady-state conditions. During this baseline test, the system did not reach steady state until the last two hours of the four hour data collection period.

# OXYGEN COMBUSTION SYSTEM TEST AT KILN FEED END

Three tests (7 to 9 hours each) were conducted with the LINDE OCS burner located at the kiln feed end, firing countercurrently to the main air burner, at final ash temperatures of  $482^{\circ}C$  (900°F) and one test (4 to 5 hours) at a final ash temperature of  $593^{\circ}C$  (1100°F). Tables 2a and 2b summarize the test results and include the previous baseline test data as a ready reference.

The data for the 482°C (900°F) ash temperature cases (Tests 1a, 2a, 3a) indicate a total of approximately  $9.1 \times 10^6$  W (31 MMBtuh) was fired in the OCS and kiln main air burner during all three tests. Different individual burner firing rates were used for each test, but the total firing rates were kept approximately equal for all three runs and the baseline case. Different stoichiometric oxygen ratios were used for each of the three tests to evaluate the impact of this parameter. The data also indicate the firing rate for the three tests was approximately 10 percent greater than the baseline test.

The steady-state capacity ranged from 9.4 to 10.9 mtph (10.4 to 12.0 tph) for the three OCS  $482^{\circ}C$  (900°F) ash temperature tests (1a, 2a, 3a). This is equivalent to 0.34 to 0.38 tons of soil per MMBtu fired, or 9 to 19 percent less capacity per MMBtu fired than the baseline case (baseline 1). The overall heat transfer efficiency for the OCS tests (1a, 2a, 3a) was decreased and ranged from 32 to 35 percent of the total energy fired or 82 to 90 percent of the baseline air burner test. The data also clearly show that the performance fell further as the firing rate of the OCS tests were reduced by 5 to 16 percent over the baseline to 50 percent of the baseline as the firing rate of the OCS tests were reduced by 5 to 16 percent over the baseline the baseline to 50 percent of the baseline to 50 percent over the baseline

Test Number	Tons/ MMBtu	MMBtu Transferred/ MMBtu Fired in the Kiln	Heat transferred to Feed W×10 <sup>6</sup> (MMBtu/h)	$NO_x$ $ppm_{dv}$ (corrected by $7\% O_2$ )	Stack Gas Flow dNm <sup>3</sup> /min (dscfm)
Baseline 1	0.42	0.39	3.2 (11.0)	63	331 (11,674)
1a	0.38	0.35	3.3 (11.2)	89	279 (9,857)
2a	0.37	0.35	3.2 (10.8)	94	314 (11,099)
3a	0.34	0.32	3.0 (10.1)	102	286 (10,105)
Baseline 2	0.31	0.34	2.8 (9.5)	67	_
1b	0.34	0.35	3.3 (11.3)	99	-

Table 2b Summary of Key Operating Conditions for Baseline and OCS Tests at Feed End

Notes:

All baseline tests were conducted with the air-natural gas burner only.

The above values are average values for each test under steady-state conditions.

The objective was to maximize the solid throughput at an average ash temperature of approximately 482°C (900°F) or 593°C (1100°F).

The average kiln rpm during the tests was 1.5 to 1.9.

Duration of each test was 7 to 9 hours except when 4- to 5-hour tests were conducted at ash discharge temperatures of approximately 593 °C (1100 °F). Oxygen consumption decreased from 1.06 to 0.63 of stoichiometric oxygen required as the OCS firing increased from  $1.2 \times 10^6$  W to  $4.1 \times 10^6$  W.

Table	a 3a Summa	ry of Key O	perating Cond	ditions for Baselin	e and OCS Tests at	Ash Dischar	ge End
						Kiln Burner	Firing Rate
Test Number	Solid Rate mtph (tph)	Moisture Content (% by dry weight)	Ash Temperature °C (°F)	Kiln Exit Gas Temperature °C (°F)	Kiln Infiltration Air dNm <sup>3</sup> /min (dscfm)	Oxygen Burner W×10 <sup>6</sup> (MM Btu/h)	Air Burner W×10 <sup>6</sup> (MM Btu/h)
Baseline 2' 2a'	12.3 (13.6) 14.3 (15.8)	17.5 17.6	479 (895) 481 (898)	732 (1350) 609 (1128)	68.5 (2420) 70.5 (2,490)	0 (0) 3.5 (11.9)	8.9 (30.4) 4.3 (14.7)

case (baseline 1) even though approximately 11 percent more energy was being fired.

The above reduced kiln heat transfer data is further supported by the higher kiln exit temperatures during the OCS tests of 86 to 178°C (188 to 353°F) over the baseline case even though kiln infiltration air increased by 1.5 to 4 percent over the baseline case due primarily to the localized aspirating effect of the OCS burner. The nitrogen oxide content in the stack gas ranged from 63 to 102  $ppm_{dv}$  (corrected to 7 percent oxygen).

The results from the single 4 to 5 hour test run (1b) with the OCS burner at the feed end at ash temperatures of approximately 593°C (1100°F) indicate that an overall heat transfer efficiency of 35 percent was achieved or 0.34 ton of soil was processed per MMBtu fired. This compares to an overall heat transfer efficiency of 34 percent or 0.31 ton of soil per MMBtu fired for the single 4- to 5-hour air burner baseline case (baseline 2) at a targeted ash temperature of 593°C (1100°F). Although the measured values indicate the OCS burner was more efficient than the baseline case relative to heat transfer efficiency and throughput per MMBtu fired the differences between the two tests were too close to differentiate with confidence. At a minimum, it is clear that there was no marked deterioration in performance between the baseline case and the OCS test at an ash temperature of approximately 593°C (1100°F).

The above discussion compares the performance of the OCS burner at the feed end firing countercurrently to the main air burner with the baseline performance of the kiln main air burner alone. Significant improved performance was anticipated due to the potentially large  $\Delta t$  between the OCS burner heat transfer zone and the moist soil feed. The visible high velocity burner flame of the OCS readily penetrated the velocity head of the countercurrent main kiln burner flue gases. However, the radiant heat portion of the flame did not significantly increase the overall heat transfer because the OCS burner transfers heat primarily by convection from the higher temperature recirculation zone.

Two theories have been postulated to explain the reduced performance that was observed during the OCS tests at the kiln feed end. Both are being studied. One theory is that the higher temperature heat transfer zone of the OCS was distorted by the main countercurrent flow of flue gases from the kiln main air burner and generally did not "see" the heat sink of the low temperature soil. As the flue gases leave the kiln and enter the hot duct, their velocity increases approximately four-fold. This increase in velocity, plus localized eddy currents, can readily destroy the effectiveness of a counterfired heat transfer source at the feed end of the kiln. The higher hot duct temperature experienced during the OCS runs also support this phenomena.

The second theory offered to explain the reduced performance is that the aspiration effect of the OCS burner created a localized vacuum [about 0.15" water column (wc) higher than normal] which induced excess air leakage through the feed belt housing. This high level of excess air leakage was detrimental. It reduced the thermal efficiency significantly of the OCS burner by dilution and shortened the penetration of the flame. In addition, the increased air infiltration rates required the operator to reduce the air burner firing rate in order to maintain the kiln vacuum. As a result, the reduction in heat transfer from the air burner more than offset the modest gain in local heat transfer from the oxygen burner.

# OXYGEN COMBUSTION SYSTEM TEST AT KILN ASH DISCHARGE END

This test phase was conducted with the OCS burner located at the ash discharge end of the HTTS rotary kiln and fired cocurrently with the kiln main air burner. The purpose of relocating the OCS burner at the ash discharge was to determine if the hot ash could be heated to final temperatures quicker while simultaneously improving heat transfer along the entire length of the kiln.

An additional baseline test (baseline 2') was run to reflect changes in baseline because the moisture in the soil stockpile was dropping due to evaporation. The results of the 3 to 4 hour baseline test (baseline 2') with the kiln main air burner were compared to a 4 to 5 hour tests (2a') with the OCS burner firing cocurrently with the kiln main air burner. Final ash

Table 3b	Summary	of Key Operating Condition	ns for Baseline and O	CS Tests at Ash	Discharge End
				NOx	
Test Number	Tons/ MMBtu	MMBtu Transferred/ MMBtu Fired in the Kiln	Heat transferred to Feed W×10 <sup>6</sup> (MM Btuh)	$ppm_{dv}$ (corrected to 7% O <sub>2</sub> )	Stack Gas Flow dNm <sup>3</sup> /min (dscfm)
Baseline 2' 2a'	0.45 0.59	0.39 0.52	3.5 (11.9) 4.0 (13.8)	56 170	329 (11,625) 300 (10,586)

Notes:

All baseline tests were conducted with the air-natural gas burner only.

The above values are actual average values for each test under steady-state conditions.

The objective was to maximize the solid throughput at an average ash temperature of approximately 482°C (900°F).

The average kiln rpm during the tests was 1.6 to 1.8.

Duration of each test was 3 to 4 hours.

Oxygen consumption during the OCS test was 0.56 of stoichiometric oxygen required.

temperatures of approximately 482°C (900°F) were targeted. Tables 3a and 3b summarize the test results.

Tables 3a and 3b indicate approximately 8.9×10<sup>6</sup> W (30.4 MMBtuh) was fired during the kiln main air burner baseline test (baseline 2') versus a combined firing rate of  $7.8 \times 10^6$  W (26.6 MMBtuh) during the OCS test. The average capacity for the baseline test was 12.3 mtph (13.6 tph) versus 14.3 mtph (15.8 tph) for the OCS test. This is equivalent to 0.45 ton processed per MMBtu for the baseline test versus 0.59 for the OCS test. Similarly, the heat transfer per MMBtu fired was 39 percent for the baseline case versus 52 percent for the OCS case. This indicates one-third more energy was transferred with the combined OCS/main air burner combination. The actual difference may be greater because the air baseline test was conducted immediately after the oxygen test when the residual refractory temperature was approximately 93°C (200°F) higher. It is postulated that the residual heat from the hot refractory may have biased the results. This is supported by the observation that the capacity leveled out at a lower rate during the last two hours of the baseline test.

During the OCS tests, the oxygen stoichiometric ratio for the OCS burner was reduced to 0.56. The infiltration air levels were within 3 percent of each other and total stack gas flow decreased by approximately 9 percent during the OCS test over the baseline case. The nitrogen oxide concentration was 56 and 170 ppm<sub>dy</sub> (corrected to 7 percent oxygen) for the baseline and OCS tests, respectively. During the subsequent tests, NO, was reduced by about 40 percent with the adjustment of the OCS oxygen nozzles. There appeared to be a tendency toward slagging of the ash approximately 4.5 m (15 ft) upstream of the discharge end of the kiln during the OCS test 2a'. However, adjustment of the oxygen nozzles to modify the flame zone recirculation characteristics effectively mitigated this problem during subsequent tests. Similar tendency toward slagging was also observed during the air baseline test (baseline 2) when the ash discharge temperature was maintained at 593°C (1100°F). Although this series of tests were of relatively short duration, a discernible capacity increase of up to approximately 16 to 22 percent was achieved by utilizing the OCS burner in conjunction with the kiln main burner at the ash discharge end.

### CONCLUSIONS

Firing the OCS burner cocurrently with the kiln main air burner is one option for increasing the capacity of the HTTS kiln on lightly contaminated soils of approximately 20 percent moisture at ash temperature of approximately 900°F. Kiln heat transfer and capacity per unit of total energy fired were 33 and 31 percent, respectively, greater than the baseline air burner test.

Firing the OCS burner countercurrently to the kiln main air burner does not appear to be an attractive option for increasing the capacity of the HTTS kiln on lightly contaminated soils of approximately 200 percent moisture at ash temperature of approximately 900°F. With the exception of one test, the heat transfer and capacity per unit of energy fired during the OCS tests were 90 and 88 percent, respectively, of the baseline test value. It does not appear the magnitude of the capacity increase for the OCS burner at the 593°C (1100°F) ash temperature can be ascertained due to limited data.

The configuration and characterization of the HTTS countercurrent kiln make it extremely improbable that any burner system located at the feed end could achieve significant capacity performance improvements. The negative impacts of infiltration air around the feed belt housing and the counterflowing flue gases from the kiln main air burner make this a very difficult location.

Matching the burner(s) heat release profile to the thermal treatment requirements of the soil substrate is required for achieving optimal heat transfer in a rotary kiln.

Emissions of nitrogen oxide fired were 41 to 203 percent greater on a dry gas basis (corrected to 7 percent oxygen) for all the OCS tests than for the baseline cases. Alteration of the LINDE "A" Burner nozzle face could modify the flame zone recirculation patterns that reduce the nitrogen oxide emission levels.

The kiln heat loss of 20.8 percent of the total heat transferred in the kiln is significant. If one-half of this heat loss was eliminated, kiln capacity could theoretically be increased by approximately 1.45 mtph (1.6 tph).

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# Air Assessment for Land Treatment No-Migration

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Air pathway assessments for three landfarm sites were conducted for compliance with the no-migration land disposal regulations. These assessments comprise of estimating the volatile and semi-volatile emissions from sludge application using the CHEMDAT model and estimating particulate emissions during application and tilling using the Fugitive Particulate Matter Air Emissions Guidance. Ambient concentrations at the unit boundary were predicted using the ISC dispersion models. Ambient air monitoring during application and tilling was included as a check on the emission and dispersion models.

### INTRODUCTION

RCRA regulations significantly restrict land disposal of refinery and other wastes. Although the effectiveness of the land treatment technique has been well demonstrated for disposal of refinery sludges [1, 2, 3], these RCRA regulations limit its use unless no-migration of hazardous materials beyond the facility unit boundary can be shown. EPA has established a rather complex procedure to obtain a "No-migration" variance which is necessary for continued application of hazardous waste unless the waste is pretreated to meet EPA standards [4]. In general, the requirements include prediction of the toxic and carcinogenic hazards to the surroundings from surface water runoff, ground water migration, and air dispersion. This paper focuses on the procedures and analysis techniques for the air pathway assessment.

Landfarming allows treatment of the constituents in refinery wastes in several different ways. Volatiles in the waste are partially vaporized and partially biodegraded. Semi-volatiles in the waste are, in general, biodegraded. Metals are immobilized within the landfarm soil by ion-exchange, formation of insoluble precipitates, and other mechanisms.

The three landfarm sites evaluated were the Rogers Landfarm, located in Centreville, Mississippi, the Baytown Refinery North Landfarm, located in Baytown, Texas, and the Billings Refinery New South Landfarm, located in Billings, Montana.

### EMISSIONS

The most important factor affecting the emissions rate of volatile components in the sludge is the application technique. Surface application usually leads to almost complete vaporization of the volatile constituents in the sludge. Subsurface application results in a significantly reduced fraction vaporized, especially for the higher molecular weight compounds. Since the waste is covered by soil, biodegradation becomes a primary mechanism for removal of the volatile constituents. Other factors affecting the emissions rate are ambient temperature and the soil characteristics, particularly grain size and moisture content.



FIGURE 1. Emissions modeling using CHEMDAT.



FIGURE 2. Landfarm oil film model.

The CHEMDAT model is currently recommended by EPA for estimating the emissions rate of volatiles from a land treatment facility [5]. Emissions can occur during several phases of waste application. As shown in Figure 1, for emissions during initial application, the waste application model is used. For the period after the initial application and prior to tilling of the waste to incorporate it into the treatment zone, the oil film model is used. Emissions after the waste is tilled into the treatment zone are estimated using the land treatment model.

Benzene is the volatile component of greatest interest, as it is the most volatile and is also a carcinogen. Figure 2 shows the fraction of benzene vaporized after application based on the oil film model. It is apparent that almost all of the benzene originally in the sludge is predicted to be vaporized unless tilling of the waste into the treatment zone is accomplished immediately after application. This is especially critical at higher windspeeds and temperatures.

The land treatment model predicts that about half of the benzene remaining in the sludge when tilled will be vaporized, depending on the climatological conditions. Thus, even for subsurface application of the sludge, emissions are about 50 percent. For surface application, essentially all of the benzene originally in the sludge can be emitted based on the combined predictions of the oil film and land treatment models.

Particulate emissions result mostly from vehicular activity on the landfarm site. This includes application and incorporation of the sludge as well as periodic tilling of the plots. Emissions during the application period tend to be reduced due to the high moisture content of the waste as it is applied. Particulate emissions also result from vehicular traffic on site roads, although boundary concentrations from these emissions are very dependent on road location and frequency of use.

The particulate emission mechanism is the primary pathway for both the semi-volatiles and metals in the sludge, and EPA has developed detailed calculation procedures to estimate these rates [6]. The major controlling factors are the silt and moisture contents of the soil as well as the speed, weight, and size of the vehicles.

### **DISPERSION MODELING**

The most important factors affecting the dispersion of emissions from landfarm sites are the wind speed, direction, and atmospheric stability class. The predicted annual average unit boundary concentrations due to emissions from the three landfarm sites were obtained using the Industrial Source Complex (ISC) Long Term dispersion model (ISCLT), from the UNAMAP6 group of EPA computer programs [7]. Two separate sets of simulations were required to predict the maximum concentrations at the unit boundary for each site. In order to determine the general location of the predicted maximum concentrations, initial simulations were made by modeling each of the sites as a number of square area sources, using Cartesian coordinates with receptors surrounding the site at 100 meters from the unit boundary. These initial simulations were then followed by another set of simulations where, in each case, the area sources which were closest to the location of the predicted maximum concentrations were divided into smaller segments in order to obtain concentrations close to the unit boundary.

A number of options are available for running the ISCLT dispersion model. Those chosen were based on the specifies of the site locations and modeling requirements. Dispersion coefficients were chosen based on the land use and population criteria of the area surrounding the landfarm sites. The regulatory default was chosen, which results in defaults for the wind profile exponents and the vertical potential temperature gradients. The regulatory default also sets several other options which are, in general, more applicable to buoyant point sources than to area sources (use of final plume rise, stack tip downwash, and buoyancy induced dispersion).

As previously mentioned, for the initial set of simulations used to determine the general location of the predicted maximum annual average concentrations, the sites were divided into square area sources, as shown for one of the locations in Figure 3. The predicted location of maximum concentration was determined using a Cartesian coordinate system with receptors 100 meters from the unit boundary. This was followed by additional simulations with receptors located within 1 meter of the unit boundary.

For the annual average concentrations, meteorological data were used in the form of the Star statistical summary of hourly observations. For each site, data from the local National Weather Service (NWS) surface station was used as typical of the wind pattern expected at the landfarm location. Data from the Baton Rouge, Louisiana, Houston, Texas, and Billings, Montana NWS stations were used for the Rogers Landfarm, the Baytown Landfarm, and the Billings Landfarm, respectively. In the initial modeling to determine the location of the predicted maximum concentration, meteorological data from the year 1987 were used.

Mixing heights for each of the sites were estimated from Holzworth [8]. The procedures in the ISC manual for assigning mixing heights, based on the Holzworth mean afternoon and morning mixing heights, were used to set the values for the six atmospheric stability classes. The annual average temperature for each landfarm location was used [9, 10, 11].

In the first simulation to locate the sector at each site where the maximum annual average concentration was predicted, Cartesian coordinate receptors were located 100 meters from the unit boundary, spaced 25 meters apart. All modeling receptors were located at a height of 1.5 meters above the terrain to be representative of inhalation height. The maximum annual

					100 Meters	
1 L = 44m	2 L = 44m	3 L = 44m	4 L = 44m	5 L = 44m		1
6	7	8	9	10	11	
L = 44m	L = 44m					
12	13	14	15	16	17	-
L = 44m	L = 44m					
18	19	20	21	22	23	
L = 44m	L = 44m					
24	25	26	27	28	29	
L = 44m	L = 44m					

FIGURE 3. Simulation of plot area sources.

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FIGURE 4. Division of plots nearest predicted maximum concentration (coordinates in meters).

average concentration for the site shown in Figure 3 is predicted to occur in a generally Southeast direction.

In order to predict unit boundary concentrations within one meter of the active plot at the landfarm shown in Figure 3, the original area sources 26, 27, 28 and 29, which are nearest the maximum concentrations predicted in the preliminary modeling, were sub-divided into 8.8 meter square area sources as shown in Figure 4. Discrete modeling receptors were located along a line one meter from the unit boundary on the edge of original sources 26, 27, 28 and 29, 1.5 meters above the terrain, and at a spacing of 10 meters.

In order to simulate an average annual concentration, the annual average emission rate assuming uniform application of sludge to the entire landfarm area was used. During normal operation, sludge will be applied on a rotating basis among several different plot areas at each of the landfarm sites.

Annual concentrations at the unit boundary were determined for the years 1983 through 1987 using the Star statistical summary meteorological data. As per the EPA suggested methodology, final concentrations were obtained by multiplying the modeling results by 1.4 to correct for the wind velocity profile since meteorological measurements were made at 10 meters and the source is at ground-level. Neutral atmospheric stability is assumed in this correction.

Short term (24-hour) emission and dispersion estimates are required for comparison to ambient air monitoring data. This comparison can be used to develop a correction factor for the annual modeling results. Short term ambient concentration predictions are obtained using the Industrial Source Complex (ISC) Short Term dispersion model (ISCST), from the UNAMAP6 group of EPA computer programs [7]. Only a single plot area of the landfarm receives sludge during the monitoring period.

In the modeling, discrete receptors are located at the monitoring points. These receptors are located 1.5 meters above the local terrain to be representative of inhalation height. As with the modeling to obtain the annual average concentrations, final concentrations are obtained by multiplying the modeling results by 1.4 to correct for wind measurements being made at 10 meters and a ground-level source.

The ambient air monitoring study must be conducted during "reasonable worst case" emissions and dispersion conditions. This requires some analysis of the climatology records (e.g., average temperature, precipitation) representative of the location of the facility. In general, the highest temperature period will result in the worst emissions case for volatiles and the driest period will result in the worst emissions case for particulates. Analysis is also required to determine if there are any worst case dispersion periods during the year. The worst operating conditions for volatile emissions will be during application and the worst operating conditions for particulates emissions will be during tilling.

EPA requires that monitors be placed so as to measure the highest ambient concentrations. These locations can be determined using dispersion modeling with the predicted meteorological conditions. Since a series of 24-hour samples is necessary, this would require placement of monitors at different distances from the plot to measure both the highest day and night concentrations. However, since daytime emissions are expected to be much higher than those at night, monitors should be placed to best observe the daytime emissions.

Recently, results from preliminary studies comparing the predicted and measured ambient concentrations of several volatile compounds at the boundary of a land treatment facility were reported [12, 13]. These studies indicated that, although some correlation of the data was possible, non-idealities in the site operation might tend to make comparison to obtain the required correction factor more difficult.

### DISCUSSION

Two parts of the air pathway assessment procedure for the No-migration demonstration warrant more detailed examination. The first is the required ambient air monitoring of sites which have been shown by waste analysis, emissions modeling and dispersion modeling to meet the No-migration healthbased concentration requirements. The second involves the minimum applicable size of the individual area sources and the validity of the model used to simulate a landfarm site. Both of these issues will require further clarification by EPA in order to establish a meaningful and consistent protocol for considering the air pathway assessment of No-migration petitions.

In the case of ambient air monitoring at the unit boundary, it is often difficult to obtain meaningful information due to both the low concentrations expected from landfarm emissions as compared to the background concentration, and the detectability of compounds in the sludge. Since many landfarm sites are located in or near large petroleum or petro-chemical facilities, the background concentration of benzene, as well as other volatile organics, can be well above the health-basedlimit required to satisfy the No-migration demonstration requirements  $(0.12 \ \mu g/m^3)$ . For any landfarm site which is predicted by dispersion modeling to be in compliance, this, combined with the typical accuracy in monitoring, results in only being able to obtain measurements of background concentrations, rather than the concentrations due to the landfarm emissions.

Even in remote areas, measurement of benzene concentrations due to landfarm emissions meeting the no-migration requirements may be futile. For example, one of the landfarm sites we evaluated, Rogers Landfarm, was in Centreville, Mississippi. The landfarm is far removed from industrial sources of benzene, in addition to being several miles from any heavily traveled roads. Preliminary benzene concentrations measured at the unit boundary of Rogers landfarm were found to be essentially equal to the background concentration which averaged 1.61  $\mu$ g/m<sup>3</sup> [14]. This compared favorably with the results of an API study of background ambient benzene concentrations [15] as well as a recently reported rural background concentration of 1.49  $\mu$ g/m<sup>3</sup> [16].

In many cases, waste analysis results indicate hazardous compounds are below analytical detection limits. These detection limits, however, may be well above concentration levels which will result in an exceedance of the health-based ambient air concentration limits. Thus, it may not be practical to undertake a monitoring program for sites where dispersion modeling predicts low concentrations relative to high background levels and the compounds of interest are not detected in the waste.

The correct minimum area source size which should be used to model the landfarm site is more of a procedural issue. EPA guidance for conducting the air part of the No-migration assessment recommends division of the area sources closest to the maximum into squares smaller than  $10m \times 10m$ . How much smaller is not addressed. The manual for the ISC program recommends that the size of area sources be at most equal to the minimum distance from a source to a receptor point to avoid over predicting concentrations [7]. For the unit boundary receptors considered in the No-migration assessment, this requires area sources of  $1m \times 1m$  or less.

While the amount of decrease in predicted concentration using smaller area sources is site specific, being dependent on the landfarm geometry and meteorology, some additional simulations of the Billings Landfarm were made dividing several of the modeled area sources into smaller than  $1m \times 1m$  sources. A reduction of over 4% in predicted concentration was found as a result of using the smaller area sources.

### CONCLUSIONS

Completion of follow up studies for these landfarm sites is still underway. These studies include additional ambient air monitoring as well as responses to Notices of Deficiency on the initial No-migration variance petitions. After completion, and review by EPA, there is a public comment period. Since the land disposal of waste is such a contentious issue (landfarming has been classified as land disposal rather than treatment), it is likely that final determination regarding Nomigration variances for operating land treatment facilities will be based on political as well as technical issues.

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# Biological Process Design and Pilot Testing for a Carbon Oxidation, Nitrification, and Denitrification System

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In response to a new NPDES permit incorporating Organic Chemical, Plastic, and Synthetic Fiber (OCPSF) effluent limits for BOD (carbonaceous and nitrogenous), TSS, and priority pollutants, a treatability study was conducted to establish design criteria for a new process wastewater treatment plant for DSM Chemicals North America, Inc. The permit also requires partial removal of total nitrogen. Based on the discharge criteria, a two-stage biological process configuration was selected. The configuration consisted of an anoxic followed by an aerobic reactor with mixed liquor recirculation. To establish design criteria, a two-phase study was conducted. The first phase involved determining wastewater characteristics and kinetic and stoichiometric coefficients. These values were used as input to "Simulation of Single-Sludge Processes" (SSSP), a computer model that was used to evaluate potential process configurations. In the second phase, a pilot-scale system was operated to verify performance. With a volume distribution of 40 percent anoxic and 60 percent aerobic and a recirculation ratio of 2, BOD, COD, and total nitrogen removal efficiencies of 99, 88, and 80 percent were obtained, respectively. Approximately 84 percent of the biodegradable COD was removed through denitrification.

### INTRODUCTION

### Background

DSM Chemicals North America, Inc., Augusta, Georgia, manufactures caprolactam and generates process wastewater containing 3,400 mg/l of chemical oxygen demand (COD) and 660 mg/l of total nitrogen. The new process wastewater NPDES permit will incorporate stringent Organic Chemical, Plastics, and Synthetic Fibers (OCPSF) industrial subcategory effluent limits for biochemical oxygen demand (BOD) (carbonaceous and nitrogenous), total suspended solids (TSS), and priority pollutants. In addition to OCPSF requirements, the permit requires partial removal of total nitrogen. Because the existing single-stage aerobic biological treatment system could not be upgraded to meet the new permit requirements cost effectively, a new system will be constructed. A two-stage single-sludge carbon oxidation, nitrification, and denitrification system was



FIGURE 1. Two stage single-sludge anoxic/aerobic configuration for carbon oxidation, nitrification and denitrification.

selected based on the need to reduce total nitrogen and the desire to minimize oxygen and alkalinity requirements. The system will consist of an anoxic reactor followed by an aerobic reactor with mixed liquor recirculation as presented in Figure 1.

To develop design criteria, a treatability study was conducted. The study included lab-scale testing, computer-aided process simulation, and pilot-scale testing. Simulation was an integral part of the study program because of the complexity of the biological system. It was performed with SSSP [J], a program based on the mathematical model for single sludge systems developed by a task group of the International Association for Water Pollution Research and Control (IAWPRC) [2] SSSP was chosen because it has been shown to accurately describe the performance of systems incorporating carbon oxidation, nitrification, and denitrification [3].

The IAWPRC model incorporates eight reactions operating on 13 components. With respect to microorganism growth and decay, reactions include the aerobic and anoxic growth of heterotrophs, aerobic growth of autotrophs, and decay of heterotrophs and autotrophs. Biochemical reactions include ammonification of soluble organic nitrogen, hydrolysis of entrapped organics, and hydrolysis of entrapped organic nitrogen. Components are classified as organics, microorganisms, nitrogen, oxygen, and alkalinity. Organics include soluble organics (readily biodegradable), particulate organics (slowly biodegradable), particulate products, and inert particulates. Microorganisms are either heterotrophs or autotrophs. Nitrogen includes soluble ammonia, nitrate/nitrite, soluble organic nitrogen (readily biodegradable), and biodegradable particulate organic nitrogen (slowly biodegradable). All nitrogen species are expressed as nitrogen equivalents. Both organic and microorganism components are expressed as equivalent amounts of COD to facilitate development of mass balance equations. All components are linked through the appropriate kinetic and stoichiometric relationships using a matrix format [2,4].

An important aspect of the IAWPRC model is the focus on prediction of activated sludge concentrations and electron acceptor (oxygen and nitrate) requirements rather than substrate removal. The rationale of the IAWPRC task group was that because of the long solids retention time (SRT) incorporated into the design of most biological treatment systems, differences in effluent soluble biologradable substrate concentration

	Average Day	
Parameter	Concentration (mg/l)	Maximum/Average Ratio
COD	3,390	2.00
BOD	1,695	2.53
TKN	362	3.72
NH3-N	226	4.18
NO <sub>3</sub> -N	299	2.14
Total Nitrogen	662	3.01
PO <sub>4</sub> -P	49	3.76
Benzene	54	b
Toluene	39	b
Phenol	3.2	b
TSS	22	b
VSS	10	b
Alkalinity (as CaCO <sub>3</sub> )	200	b
pH <sup>e</sup>	6.1	11.8

pH units, S.U.

<sup>b</sup>Insufficient data to establish meaningful ratio

Parameter	Maximum Monthly Average (mg/l)	Maximum Day (mg/l)
BOD	34 <sup>a</sup>	92ª
TSS	49	159
Total Nitrogen	330	826
Benzene	0.037	0.136
Toluene	0.026	0.080
Phenol	0.015	0.026

between different system configurations are relatively small. Conversely, large differences in activated sludge concentrations and electron acceptor (oxygen and nitrate) requirements are common [2]. Furthermore, nitrogen removal is greatly influenced by activated sludge concentration and electron acceptor requirements, but influenced little by effluent soluble biodegradable substrate concentration.

### **OBJECTIVE AND APPROACH**

A phased and iterative approach was taken. In the first phase, the pilot plant was started and selected wastewater characteristics and kinetic and stoichiometric coefficients were determined in lab-scale experiments.

In the second phase, SSSP simulations were performed using experimentally determined wastewater characteristics and kinetic and stoichiometric coefficients. These simulations were used to aid in the selection of the pilot plant configuration to be tested. The pilot plant was reconfigured and a 30-day test run was conducted.

The first-phase objective was to determine the following parameters:

- Heterotrophic yield
- heterotrophic decay coefficient
- Anoxic growth and hydrolysis factors
- Maximum specific growth rate coefficient of nitrifiers
- Readily biodegradable COD concentration

The second-phase objective was to verify the performance of the pilot plant.

### WASTEWATER CHARACTERISTICS AND PER-MIT REQUIREMENTS

Table 1 presents the historical average process wastewater characteristics and the ratios of maximum to average day load for each parameter. The COD to total nitrogen ratio is approximately five, indicating that a substantial portion of the COD could be removed through denitrification. The maximum-to-average day ratios indicate that the reduced nitrogen (TKN) load is highly variable compared to the COD load.

The new NPDES permit requirements are presented in Table 2. Based on the wastewater characteristics, monthly average BOD and total nitrogen removals of greater than 98 and 50 percent are required, respectively. Benzene and toluene removals of greater than 99.9 percent are required. Phenol removal of greater than 99.5 percent is required.

### DESCRIPTION OF EXPERIMENTS AND DISCUS-SION OF RESULTS

### **Initial Simulations and Pilot Plant Startup**

### Simulations

Because the lab-scale experiments require a stable nitrifying and denitrifying sludge acclimated to the wastewater to be

Symbol	Definition	
Symoor		
YA	Yield of autotrophic biomass	
Y <sub>H</sub>	Yield of heterotrophic biomass	
$f_p$	Fraction of biomass leading to particulate products	
i <sub>XB</sub>	Mass of nitrogen per mass of COD in biomass	
i <sub>XP</sub>	Mass of nitrogen per mass of COD in products from	
	biomass	
μ <sub>Hm</sub>	Maximum specific growth rate for heterotrophic biomass	
Ks	Half-saturation coefficient for heterotrophic biomass	
К <sub>о.н</sub>	Oxygen half-saturation coefficient for heterotrophic biomass	
K <sub>NO</sub>	Nitrate half-saturation coefficient for denitrifying	
	heterotrophic biomass	
b <sub>H</sub>	Decay coefficient for heterotrophic biomass	
η	Correction factor for $\mu_{Hm}$ under anoxic conditions	
78 NL	Correction factor for hydrolysis under anoxic conditions	
k.	Ammonification rate	
<i>k</i> .	Maximum specific hydrolysis rate	
K <sub>v</sub>	Half-saturation coefficient for hydrolysis of slowly	
*	biodegradable substrate	
	Maximum specific growth rate for autotrophic biomass	
K	Ammonia half-saturation coefficient for autotrophic	
I NH	hiomass	
V	Owner half saturation coefficient for autotrophic highers	
h <sub>O,A</sub>	Descu coefficient for extensible biomese	
U <sub>A</sub>	Decay coefficient for autotrophic biomass	

Symbol	Units	Default Value	Assumed Value
toichiometric Param	eters		
YA	g cell COD formed (g N oxidized) <sup>-1</sup>	0.24 <sup>a</sup>	
Y <sub>H</sub>	g cell COD formed (g COD oxidized) <sup><math>-1</math></sup>	0.67	0.45
$f_p$	dimensionless	0.08"	
i <sub>xB</sub>	g N(g COD) <sup>-1</sup> in biomass	0.086"	
i <sub>XP</sub>	$g N(g COD)^{-1}$ in products from biomass	0.06"	
inetic Parameters			
$\mu_{Hm}$	day <sup>-1</sup>	4.0	
Ks	$g \text{ COD } m^{-3}$	10	
K <sub>O,H</sub>	$g O_2 m^{-3}$	0.104	
KNO	$g NO_3 - N m^{-3}$	$0.20^{a}$	
b <sub>H</sub>	day <sup>-1</sup>	0.62	0.10
η	dimensionless	0.8	
$\eta_h$	dimensionless	0.4	
k <sub>a</sub>	$m^3$ (g cell COD · day) <sup>-1</sup>	0.16	
k,	g slowly biodegradable COD (g cell		
0.105	COD·day) <sup>-1</sup>	2.2	
Kx	g slowly biodegradable COD (g cell		
	COD) <sup>-1</sup>	0.15	
H Am	dav <sup>-1</sup>	0.65	0.30
K <sub>NH</sub>	g NH2-N	1.0	
KoA	$g O_2 m^{-3}$	1.04	
b	dav <sup>-1</sup>	0.12	0.03

treated, it was necessary to start the pilot plant before the actual configuration to be tested was selected. To aid in the selection of the initial pilot plant configuration, simulations were performed using historical wastewater characteristics and assumed kinetic and stoichiometric coefficients.

Table 3 defines the kinetic and stoichiometric parameters used in the model. Table 4 presents the units and default values for these parameters [1]. For the initial simulations, default values were used with the exceptions of the assumed values listed in Table 4. It was believed that the assumed values would be more accurate than the default values for DSM wastewater. Historical data were used to define the initial simulation wastewater characteristics as presented in Table 5. It was assumed that 80 percent of the COD was biodegradable and that of the biodegradable COD, 25 percent was soluble (readily biodegradable). Similarly, organic nitrogen was assumed to be 80 percent biodegradable with 25 percent soluble and 75 percent particulate.

Several alternative process configurations were evaluated at a 30-day SRT. This relatively long SRT was selected because the effect of wastewater constituents on nitrification were unknown and a stable nitrifier population was required. A feed flow rate of 52 l/day was selected based on a target reactor mixed liquor volatile suspended solids (MLVSS) of approximately 4,500 mg COD/l (approximately 3,000 mg VSS/l). Figure 2 presents SSSP input and output for the initial pilot plant configuration chosen. The reactor volumes and flow rates presented are 1,000 times greater than the pilot plant values because SSSP accepts only whole numbers. Under the section entitled "Steady-State Solution" the column headed by the number 1 describes the anoxic reactor contents, and the column headed by number 2 describes the aerobic reactor contents (or unclarified effluent). A small anoxic reactor volume relative to the aerobic reactor volume was selected for startup to promote development of a stable nitrifier population. Recirculation was not required with this configuration because of the excess nitrate concentration in the anoxic reactor. A recycle

Symbol	Constituent Definition	Units	Historical Value	
XRH	Heterotrophic organisms	g COD m <sup>-3</sup>	0	
XRA	Autotrophic organisms	$g \text{ COD } m^{-3}$	0	
X <sub>P</sub>	Particulate organics	g COD m <sup>-3</sup>	0	
$X_I$	Inert particulates (organics)	$g \text{ COD } m^{-3}$	0	
Xs	Particulate organics	$g \text{ COD } m^{-3}$	2034	
Ss	Soluble organics	$g \text{ COD } m^{-3}$	678	
SNH	Soluble ammonia N	$g N m^{-3}$	226	
SNO	Soluble nitrate/nitrate N	$g N m^{-3}$	299	
SND	Soluble organic N	$g N m^{-3}$	27	
X <sub>ND</sub>	Biodegradable particulate organic N	$g N m^{-3}$	82	
So	Oxygen	$g O_2 m^{-3}$	0	
SALK	Alkalinity	mole m <sup>-3</sup>	100	

### PROCESS CONFIGURATION AND FLOW DISTRIBUTION

	1	2	
-	30	170	
-	1.00	0.00	
-	0.00	2.00	
=	52	0	
-	0	0	
-	*	*	
		$ \begin{array}{c} 1 \\ = 30 \\ = 1.00 \\ = 0.00 \\ = 52 \\ = 0 \\ = * \\ \end{array} $	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

		ST	EADY	-ST/	TE SO	LUTION	
CONSTITUENTS					FEED	1	2
Heterotrophic Organisms	g	cod	m-3	=	0.0	3509.0	3456.4
Autotrophic Organisms	ġ	cod	m-3		0.0	261.4	281.8
Particulate Products	ġ	cod	m-3	-	0.0	810.3	857.1
Inert Particulates	q	cod	m-3	-	0.0	0.0	0.0
Particulate Organics	q	cod	m-3	-	2034.0	666.1	54.0
Soluble Organics	ģ	cod	m-3	=	678.0	1.3	0.2
Soluble Ammonia N	ģ	n	m-3	=	226.0	116.8	0.6
Soluble Nitrate/Nitrite N	ġ	n	m-3	=	299.0	112.6	247.2
Soluble Organic N	ġ	n	m-3	-	27.0	0.2	0.1
Biodegrad Part Organic N	ġ	n	m-3	=	82.0	30.2	3.5
Oxygen	ġ	02	m-3	=	0.0	0.0	2.0
Alkalinity	mo	le	m-3	-	1.0	6.5	-11.4
MLVSS	q	cod	m-3	-		5246.8	4649.2
02 Consumed g d	52	m-3	d-1	=		0.0	744.0
Nitrate Consumed g no3-	-n	m-3	d-1	=		556.3	5.2

FIGURE 2. Simulation for initial pilot plant configuration (20°C).



FIGURE 3. Pilot plant process flow diagram.

*: 	Table 6 Pilot Plant Analytical Schedule									
			Sample L	ocation				Testing Freq	uency	
Parameter	Influent (1)	Anoxic Reactor (2)	Aerobic Reactor (3)	Waste Sludge (4)	Effluent (5)	Recyle (6)	Daily	Alternate Days	Bi-Weekly	Analytical Method [5,6]
COD	х			Xª	х		Х			EPA 410.1
SCOD	x	х			X			х		EPA 410.1
BOD					X			х		EPA 405.1
CBOD	x				х			Х		EPA 405.1
SBOD					х			X		EPA 405.1
TKN	х	х		Xª	х		Х			EPA 351.3
NH3-N	х	х			X		Х			SM 417E
NO <sub>2</sub> -N		х			x	х	Х			EPA 354.1
NO3-N	х	х			х	х	X			EPA 353.3
PO₄-P	х		2		х				х	EPA 365.3
TSS	х	х	х	х	х		х			EPA 160.2
VSS	х		х						х	EPA 160.4
Alkalinity	х	х	х		х		Х			EPA 310.1
pН	х	х	х		х		Х			EPA 150.1
OUR			х				Х			SM 213A
SVI			х					х		SM 213C
DO		х	х				х			EPA 360.1
Temperature			х				х			EPA 170.1
Benzene	х				X <sub>b</sub>			х		EPA 602
Toluene	х				X <sup>b</sup>			х		EPA 602
Phenol	х				x			х		EPA 604
Microscopic Observation			x						х	-
'Di weeklu										

"Analyzed during startup only

flow rate equal to the feed flow rate was used throughout the study.

### Materials

Figure 3 presents the pilot plant process flow diagram. The anoxic and aerobic reactors were 55-gallon cylindrical polyethylene tanks. The anoxic reactor had a liquid volume of 30 liters and was mixed using a variable speed mixer. The aerobic reactor had a volume of 170 liters and was mixed and aerated with compressed air. The secondary clarifier consisted of an inverted, open-top, 20-liter cylindrical carboy. The clarifier was fitted with a 4-inch-diameter stilling well which received mixed liquor; a polypropylene funnel which served as the overflow weir; and a rake arm driven by a variable speed motor. All pumping was performed with peristaltic pumps. Waste sludge was automatically pumped from the aerobic reactor on a 1-hour cycle. Alkalinity was supplied to the aerobic reactor with a manually controlled piston metering pump when required. Clarifier effluent was pumped to a mechanically mixed 1-liter Erlenmeyer flask which served as a composite sample sump. A refrigerated ISCO sampler was used to collect an effluent sample on a 15-minute cycle. Flask overflow was pumped to an effluent tank for daily volume measurement.

### Methods

The pilot plant was seeded with biomass from the existing WWTP and operated for approximately 10 weeks before the

test run began. A 24-hour composite process wastewater sample was collected daily in a 55-gallon drum to serve as the pilot plant influent. The influent flow rate was constant during each run. Dynamic pollutant loadings were the result of daily variations in pollutant concentrations. The reactor temperatures were targeted for the anticipated full-scale minimum monthly average temperature of approximately 20°C. Provisions were not made to cool the reactors when slightly higher temperatures were periodically encountered. Table 6 presents the pilot plant analytical schedule during startup and testing. Analyses were performed in accordance with established procedures [5,6].

### WASTEWATER CHARACTERISTIC AND KINETIC AND STOICHIOMETRIC COEFFICIENT DETER-MINATION

Because most of the kinetic and stoichiometric parameters presented in Table 4 are either near constants  $(Y_A, f_p, i_{XB}, i_{XP}, K_{NO}, K_{O,H}, K_{O,A})$  or have minimal influence in predicting sludge generation and oxygen requirements  $(K_s, k_a, k_h, K_X, K_{NH}, b_A)$ , determination of a relatively small number of parameter coefficients will result in reasonably accurate model calibration. The following parameters are greatly influenced by wastewater composition and were determined experimentally:

 $Y_H$ —Heterotrophic yield (g COD/g COD)

- $b_H$ —Heterotrophic decay coefficient (day<sup>-1</sup>)
- $\eta_g$ —Anoxic growth factor (dimensionless)

Table	7	Test	Run	Data	for	Heterotrophic	Yield	Deter-
				r	nins	ation		

Time (hr)	VSS (mg/l)	SCOD (mg/l)
0	396	2,882
21	597	2,186
45	883	1,085
69	730	784
93	620	749
C		

 $\eta_h$ —Anoxic hydrolysis factor (dimensionless)

 $\mu_{Am}$ —Maximum specific growth rate coefficient of nitrifiers (day<sup>-1</sup>)

 $S_s$ —Readily biodegradable COD concentration (g COD m<sup>-3</sup>)

#### Heterotrophic Yield

Theory. The true heterotrophic yield  $(Y_H)$  is required to estimate the concentration of readily biodegradable COD in the influent wastewater, and to predict sludge production and oxygen requirements. This value is estimated by determining the increase in volatile suspended solids (VSS) and decrease in soluble COD (SCOD) in a batch reactor. The true heterotrophic yield is calculated using the following equation:

$$Y_H = \frac{\Delta \text{VSS}}{\Delta \text{SCOD}} \tag{1}$$

Materials. A 13-liter batch reactor with diffused aeration was used.

Methods. An aliquot of filtered influent wastewater and acclimated biomass (approximately 400 mg VSS/I) obtained from the pilot plant was placed in the reactor. The reactor VSS and SCOD concentrations were measured daily until the SCOD concentration became limiting.

**Results.** One test run was conducted to determine  $Y_H$ . Results are presented in Table 7. The increase in VSS over the first 45 hours was 487 mg/l while the decrease in COD was 1797 mg/l. The resulting yield is 0.27 mg VSS/mg COD. Assuming 1.48 mg COD/mg VSS,  $Y_H$  is 0.40 mg COD/mg COD. After 45 hours, the supply of biodegradable COD was exhausted and cell decay began to occur as the data for hours 69 and 93 indicate.

### Heterotrophic Decay

Theory. The heterotrophic decay coefficient is affected by the nature of the wastewater being treated. Therefore, it should be determined to estimate sludge production and oxygen requirements [2,7]. An indirect determination was used for this study, requiring that the true yield, observed yield, and SRT of a system operating under steady-state conditions be known. The traditional decay coefficient  $b'_H$  may then be calculated using:

$$Y_{obs} = \frac{Y_H}{1 + b'_H \theta_X} \tag{2}$$

where:

 $Y_{obs} = observed (net) yield$ 

 $\theta_{X}$  = solids retention time

As described by the IAWPRC task group [2], traditional modeling of biological systems does not incorporate the recycling of substrate from decay. Therefore, the traditional decay coefficient must be modified for use in SSSP. The modified decay

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coefficient  $(b_H)$  is calculated using:

$$b_H = \frac{b'_H}{1 - Y_H (1 - f_p)} \tag{3}$$

*Results.* The observed yield in the pilot plant at a 30-day SRT was 0.12 mg VSS/mg COD removed at an average temperature of 19<sup>°</sup>C. Based on the experimentally determined true yield of 0.27 mg VSS/mg COD, the traditional heterotrophic decay  $(b'_{H})$  calculated using equation 2 is 0.042 day<sup>-1</sup>. The modified decay coefficient calculated from equation 3 is 0.066 day<sup>-1</sup>.

### Anoxic Growth and Hydrolysis Factors

Theory. The anoxic growth factor  $(\eta_g)$  and anoxic hydrolysis factor  $(\eta_a)$  are used to predict denitrification performance [2,8]. The anoxic growth factor adjusts for either the change in growth of heterotrophic bacteria when using nitrate as the electron acceptor, or for the fact that not all heterotrophs can denitrify [2]. The anoxic hydrolysis factor adjusts for the hydrolysis of slowly biodegradable COD by heterotrophs when using nitrate as the electron acceptor.

To determine these factors, nitrate utilization rate (NUR) and oxygen utilization rate (OUR) are measured in parallel anoxic and aerobic batch reactors, respectively. When the biomass is brought into contact with the influent wastewater, the initial growth of heterotrophs results from the removal of readily biodegradable COD. When the readily biodegradable COD has been removed, the growth of heterotrophs results from the hydrolysis of slowly biodegradable COD to readily biodegradable COD. The anoxic growth and hydrolysis factors are calculated from the ratio of NUR to OUR using the following equations:



FIGURE 5. Oxygen utilization rate versus time for the determination of anoxic growth and hydrolysis factors.

	Growt	th		Hydrol	ysis	
	NURg	OURg		NUR <sub>h</sub>	OUR <sub>h</sub>	
Run	(mg NO <sub>3</sub> -N/1/hr)	(mg O <sub>2</sub> /1/hr)	$\eta^a{}_g$	(mg NO <sub>3</sub> -N/1/hr)	(mg O <sub>2</sub> /1/hr)	$\eta^a{}_h$
1	41	139	0.84	27	110	0.70
2	60	176	0.98	31	138	0.64
3	60	148	1.0 <sup>b</sup>	25	100	0.72
Average			0.94			0.69

<sup>b</sup>Calculated value equals 1.16, however, maximum theoretical value 1.0.

$$\eta_h = \frac{2.86 \times \text{NUR}_g}{\text{OUR}_g} \tag{5}$$

Materials. Two 9.0-liter mechanically mixed batch reactors were used. The anoxic reactor was sealed and nitrogen gas was continually added to the reactor headspace and vented to assure that oxygen was not present. Compressed air was delivered through two gas diffusing stones in the aerobic reactor.

Methods. The reactors were seeded with 5 liters of biomass from the pilot plant anoxic reactor before each test. The biomass was then contacted with influent wastewater volumes ranging from 0.75 to 1.5 liters. Depending on the wastewater nitrate concentration, 0.1 or 0.2 liter of 1,000 mg/l NO<sub>3</sub>-N standard was also added to maintain nonlimiting NO<sub>3</sub>-N concentrations. DO was continuously monitored in the anoxic reactor to verify that none was present. Samples were obtained from each reactor at 10- to 15-minute intervals for 2 to 3 hours. The samples were filtered before analysis. Anoxic reactor pH, temperature, and MLVSS, NO<sub>3</sub>-N, NO<sub>2</sub>-N, SCOD, and alkalinity concentrations were determined at various intervals. Only OUR was determined in the aerobic reactor.

Results. Plots of NO<sub>3</sub>-N and OUR versus time for one test run are presented in Figures 4 and 5, respectively. The plots indicate that the readily biodegradable COD in both reactors was removed after approximately 40 minutes, after which there was a distinct decrease in both NUR and OUR. Table 8 presents a summary of the results for the three test runs. The average anoxic growth and hydrolysis factors were 0.94 and 0.69, respectively.

### Maximum Specific Growth Rate Coefficient of Nitrifiers

Theory. The maximum specific growth rate coefficient of nitrifiers  $(\mu_{Am})$  is highly dependent on constituents in the wastewater and must be determined to predict nitrification performance [2]. Since nitrifying bacteria grow at a much slower rate than heterotrophic bacteria, the minimum SRT in



FIGURE 6. Natural logarithm of NO<sub>2</sub>-N versus time for the determination of maximum specific growth rate of *Nitrosomonas*.

nitrifying systems is dependent on  $\mu_{Am}$ . Once  $\mu_{Am}$  is determined, an appropriate SRT with a reasonable factor of safety can be selected. To determine  $\mu_{Am}$ , nitrifying biomass from a system treating the wastewater is placed in a batch reactor and diluted with system effluent. Nonlimiting NH<sub>3</sub>-N concentrations should be maintained for several days. In an environment with a relatively low concentration of nitrifying bacteria and nonlimiting NH<sub>3</sub>-N concentrations, the nitrifying bacteria will grow at their maximum rate, making oxidized nitrogen production (NO<sub>2</sub>·N + NO<sub>3</sub>-N) proportional to the mass of nitrifying bacteria. A plot of the natural logarithm of the oxidized nitrogen concentration versus time will give a straight line with a slope equal to  $\mu_{Am}(2)$ .

Materials. A 12-liter batch reactor with diffused aeration was used. An automatic pH controller was used to maintain reactor pH. Alkalinity was supplied using a peristaltic pump.

Methods. An aliquot of pilot plant effluent and acclimated pilot plant biomass (approximately 400 mg VSS/I) was placed in the reactor. Ammonium chloride was added to provide an initial NH<sub>3</sub>-N concentration of approximately 300 mg/l. The reactor DO was maintained at 4 mg/l. Reactor pH was monitored continuously, and a concentrated stock solution of sodium bicarbonate was automatically delivered to the reactor when the pH fell below 7.2. Dry sodium bicarbonate was added directly to the reactor as needed to meet major alkalinity requirements. Reactor temperature, pH, and soluble TKN (STKN), NH<sub>3</sub>-N, NO<sub>2</sub>-N, NO<sub>3</sub>-N, and SCOD concentrations were measured daily until the NH<sub>3</sub>-N concentration became limiting.

Results. High NH<sub>3</sub>-N concentrations in the reactor resulted in inhibition of Nitrobacter and a buildup of NO<sub>2</sub>-N. This did not interfere with  $\mu_{Am}$  determination since the growth rate of Nitrosomonas is the rate-limiting step in the conversion of ammonia to nitrate. The plot of the natural log of NO<sub>2</sub>-N concentration versus time for the single test run conducted is presented in Figure 6. The slope of the line is 0.36 day<sup>-1</sup> at 20°C. This value agrees with reported literature values ranging from 0.34 to 0.65 day<sup>-1</sup> [2].

### Readily Biodegradable COD

Theory. An estimate of readily biodegradable COD in the influent wastewater is required to predict sludge production, oxygen requirements, and organic and nitrogen removals. The concentration of readily biodegradable COD  $(S_0)$  is estimated by measuring the change in OUR in a completely mixed reactor with a square wave loading condition. The reactor is operated at an SRT of approximately 2 days, and the square wave loading condition consists of an alternating 12-hour on/off feed. The change in OUR shortly after feed termination is associated with the removal of readily biodegradable COD. A detailed theoretical discussion of the readily biodegradable COD test is presented by Ekama *et al* [9]. The concentration of readily biodegradable COD is calculated using the following equation:



FIGURE 7. Response of completely mixed reactor to a 12-hour square wave load for the determination of readily biodegradable COD.

Readily Biodegradable COD 
$$(mg/l) = \frac{\Delta OURV}{Q(1-Y_H)}$$
 (6)

where:

 $\Delta OUR$  = change in OUR after feed termination (mg/l/hr) V = reactor volume (l)

Q = feed flow rate prior to termination (l/hr)

Materials. A 9.8-liter completely mixed reactor with an internal clarifier and solids recycle was used. Influent wastewater delivery and solids wasting were performed using variablespeed peristaltic pumps operated by a programmable controller. Compressed air was delivered through two gas diffusing stones.

Methods. A 24-hour composite sample of influent wastewater was collected daily and used as feed to the reactor. The reactor was seeded with biomass from the existing WWTP and operated under constant flow and load conditions for approximately 3 SRTs. The targeted SRT was 2.5 days. After stable OURs and VSS concentrations were obtained, a square wave loading condition was established (12-hour on/off feed). The reactor was operated under these conditions for 2 SRTs before testing began. OURs were determined every half hour for 2 hours before feed termination to obtain an average OUR. After feed termination, OURs were determined every 10 minutes for the first 30 minutes and every 30 minutes thereafter until the OUR stabilized (approximately 2 to 3 hours). The influent flow rate, reactor pH, temperature, and COD, TSS, VSS, and NH<sub>3</sub>-N concentrations were determined daily in addition to the OUR measurements.

*Results.* A plot of OUR versus time for one test run is presented in Figure 7. The plot illustrates the dramatic decrease in OUR resulting from the removal of readily biodegradable COD. Table 9 summarizes the COD data from each test run. Based on the heterotrophic yield of 0.40 mg COD/mg COD and an 88 percent biodegradable COD fraction, the average readily biodegradable COD concentration from eight test runs was 951 mg/l. This concentration represents 24 percent of the total feed COD and 28 percent of the biodegradable COD. The readily biodegradable fraction varied significantly between test runs, ranging from 6 to 51 percent of the biodegradable COD.

### SECOND PHASE

### **Simulations and Pilot Plant Reconfiguration**

### Simulations

Two sets of simulations were performed using the experimentally determined coefficients and the wastewater characteristic data obtained during initial pilot plant operation. The first set of simulations involved varying the anoxic reactor volume, reported as a fraction of total reactor volume, while holding the recirculation ratio constant at three times the feed flow rate. The second set of simulations involved varying the recirculation ratio while holding the reactor volumes constant. These simulations were used to aid in the selection of reactor volumes and a recirculation flow rate.

Initial pilot plant effluent BOD data indicated that a soluble carbonaceous BOD (SCBOD) of less than 15 mg/l would be



FIGURE 8. Effect of anoxic reactor volume fraction on anoxic reactor particulate COD, effluent NO<sub>3</sub>-N and aerobic reactor oxygen requirement.

Table 9 Summary of COD Data from Readily Biodegradable COD Tests					
Run	Influent COD (mg/l)	Biodegradable COD <sup>a</sup> (mg/l)	Readily Biodegradable COD <sup>b</sup> (mg/l)		
1	4,412	4,323	1,630		
2	3,769	3,317	436		
3	5,318	4,680	1,197		
4	4,104	3,612	217		
5	4,030	3.546	712		
6	2.825	2,486	1,272		
7	3.059	2,692	1,058		
8	3.059	2.692	1,089		
Average	3,885	3,419	951		

The biodegradable COD was assumed to be equal to 88 percent of the influent COD based on preliminary pilot data \*Calculated using equation 6



### FIGURE 9. Effect of recirculation ratio on anoxic reactor NO<sub>3</sub>-N, effluent NO<sub>3</sub>-N and aerobic reactor oxygen requirement.

required to meet the 34 mg/l total BOD limit. Since the pilot plant SCBOD had averaged 10 mg/l, it was apparent that reducing the SRT could cause the SCBOD concentration to quickly approach or exceed the 15 mg/l target. Thus, a 30-day SRT was selected for the additional pilot plant studies.

Simulation results showing the effect of varying anoxic reactor volume fraction on particulate organics (slowly biodegradable COD), effluent NO<sub>3</sub>-N, and aerobic reactor oxygen requirements at a recirculation ratio of three are presented in Figure 8. Anoxic fractions greater than 0.5 were not evaluated because sludge settleability is reported to deteriorate at higher ratios [10,11]. As the anoxic fraction approaches the maximum of 0.5, the rate of decrease in the three dependent variables declines significantly. This is the result of a growth-limiting biodegradable COD concentration in the anoxic reactor.

Selecting an anoxic and aerobic reactor volume distribution required a compromise between nitrification stability and total nitrogen removal. During startup, the pilot plant had shown slight instability with respect to nitrification, resulting in high nitrogenous BOD (NBOD). Conversely, historical data indicated that maximum month average day total nitrogen loads could be 30 percent higher than average month average day loads. High total nitrogen loads without a concurrent increase in process or supplemental wastewater COD would result in high effluent total nitrogen as nitrate. Based on these considerations, a volume distribution of 40 percent anoxic and 60 percent aerobic was selected. At this distribution the predicted effluent NO<sub>3</sub>-N concentration of 91 mg/l would result in a factor of safety of greater than 200 mg/l with respect to the effluent total nitrogen limit. With respect to nitrification, the aerobic SRT would be 18 days (0.6  $\times$  30 days). Based on  $\mu_{Am}$ of 0.36 day<sup>-1</sup>, the theoretical minimum SRT for nitrification is 2.8 days (1/0.36 day<sup>-1</sup>). Therefore, a sixfold factor of safety would be achieved for nitrification. The large factor of safety is necessary because of the highly variable TKN load and the potential for nitrifier inhibition.

Table 10 Pilot Plant Process Parameters				
	Parameter	Value		
Overall System				
	Solids Retention Time $(\theta_x)$	30 days		
	Hydraulic Retention Time	4.44 days		
	Influent Flow Rate	45 l/d		
	Organic Loading Rate $(F_a/M_p)$ (average)	0.27 mg COD/mg MLVSS/d		
	Organic Removal Rate $(F_r/M_v)$ (average)	0.24 mg COD/mg MLVSS/d		
Anoxic Reactor				
	Solids Retention Time	12 days		
	Volume	80 liters		
	Recycle Flow Rate	45 l/d		
	Recirculation Flow Rate	90 l/d		
	Actual Hydraulic Retention Time	0.44 days		
	Nominal Hydraulic Retention Time	1.78 days		
	MLSS (average)	2.771 mg/l		
	MLVSS (average)	2.466 mg/l		
	Organic Loading Rate (F./M.) (average)	0.71 mg COD/mg MLVSS/d		
	Organic Removal Rate $(F_{-}/M_{-})$ (average)	0.55 mg COD/mg MLVSS/d		
	Dissolved Oxygen (average)	0 mg/l		
Aerobic Reactor				
	Solids Retention Time	18 days		
	Volume	120 liters		
	Actual Hydraulic Retention Time	0.67 days		
	Nominal Hydraulic Retention Time	2.67 days		
	MLSS (average)	2.830 mg/l		
	MLVSS (average)	2.519 mg/l		
	SVI (average)	68  ml/g		
	Organic Loading Rate (F /M.) (average)	0.11 mg COD/mg MLVSS/d		
	Organic Removal Rate $(F/M)$ (average)	0.05 mg COD/mg MLVSS/d		
	Air Flow Rate (average)	283 1/hr		
	Dissolved Oxygen (average)	2.9 mg/l		
	Oxygen Utilization Rate (average)	22  mg/l/hr		
	Temperature (average)	21°C		
Parameter	Influent (mg/l)	Anoxic Reactor (mg/l)	Effluent (mg/l)	
------------------------------------	--------------------	--------------------------	--------------------	--
COD	3,101	_	406	
SCOD	-	463	381	
Total BOD	1,511	-	19	
SCBOD	-	-	5	
NBOD	_	_	6	
BOD <sub>TSS</sub>	—	-	8	
TKN	322	81 <sup>b</sup>	30	
NH <sub>3</sub> -N	240	63	8	
NO <sub>2</sub> -N	0	0.2	3	
NO <sub>3</sub> -N	436	67	116	
Total Nitrogen	758	148 <sup>b</sup>	149	
PO₄-P	44	_	40	
TSS	21	2,771	23	
VSS	10	2,466	20	
Benzene	27	_	<u> </u>	
Toluene	60	_	<u> </u>	
Phenol	2.4	-	< 0.01	
Acidity	100	—	—	
Alkalinity (as CaCO <sub>1</sub> )		662	270	
pH	4.11	7.8	7.5	

Not analyzed during the test run. Less than 0.01 mg/l during startup. Soluble.

Simulation results showing the effect of recirculation ratio on anoxic reactor NO<sub>3</sub>-N, effluent NO<sub>3</sub>-N, and aerobic reactor oxygen requirement at an anoxic fraction of 0.4 are presented in Figure 9. Below a recirculation ratio of two, NO<sub>3</sub>-N is limiting in the anoxic reactor. As the recirculation ratio increases, effluent NO<sub>3</sub>-N and aerobic reactor oxygen requirements increase.

The recirculation ratio plays an important role in maintaining the proper pH in each reactor, which is particularly critical when treating high-strength nitrogenous wastewaters. At low

PROCESS CONFIGURATION AND FLOW DISTRIBUTION

OVERALL PLANT SPECIFICATION Number of Reactors (up Solids Retention Time ( Average Flow Rate (m3)	ONS to day /da	9) = (s) = (y) =	- 3	2 10.0 45				
INDIVIDUAL REACTOR SPEC: Reactor Volume (m3) Feed Fraction (0 to 1) O2 Concentration (g O2/m3 Recycle Input (m3/day) Recirculation Input (m3/da Recirculation originated :	IFI ) ay) fro	CAT	IONS	::		1 80 1.00 0.00 49 2	2 0 120 0 0.00 0 2.00 5 0 0 0 *	
		ST	EAD	(-ST	ATE	SO	UTION	
CONSTITUENTS					F	EED	1	2
Heterotrophic Organisms	q	cod	m-3	. =		0.0	3215.9	3166.7
Autotrophic Organisms	q	cod	m-3	) =		0.0	178.1	188.3
Particulate Products	g	cod	m-3	. =		0.0	542.5	554.9
Inert Particulates	ģ	cod	m-3	=		0.0	0.0	0.0
Particulate Organics	g	cod	m-3	. =	19	65.0	136.2	27.2
Soluble Organics	g	cod	m-:	3 =	76	4.0	0.5	0.1
Soluble Ammonia N	g	n	m-:	3 =	24	0.0	58.0	0.8
Soluble Nitrate/Nitrite N	g	n	m-:	. =	43	6.0	57.9	118.3
Soluble Organic N	g	n	<b>m-</b> :	3 =	1	7.0	0.1	0.0
Biodegrad Part Organic N	g	n	m-:	3 =	4	3.0	4.6	1.7
Oxygen	g	02	m-:	3 =		0.0	0.0	2.0
Alkalinity	mo	le	<b>m</b> -:	3 =	-	0.5	13.5	5.1
MLVSS	g	cod	m-:	3 =			4072.8	3937.1
02 Consumed g	02	m-3	d-1	_ =			0.0	615.2
Nitrate Consumed g no3	-n	m-3	d-1				314.7	3.5

FIGURE 10. Simulation for pilot plant test run (21°C).



FIGURE 11. COD removed per unit blomass per unit time versus COD applied per unit blomass per unit time.

recirculation ratios, anoxic reactor alkalinity concentrations are typically high because of the production and buildup of alkalinity. Likewise, aerobic reactor alkalinity concentrations are typically low because of the consumption and depletion of alkalinity. This situation can result in a very high anoxic reactor pH and a very low aerobic reactor pH. By increasing the recirculation ratio, the transfer of alkalinity from the anoxic reactor to the aerobic reactor is increased, bringing the reactor alkalinity concentrations and pHs closer together. This reduces the pH-induced stress on the microorganisms as they pass from one environment to the other.

Based on considerations of wastewater variability with respect to nitrogen, COD, and alkalinity, and given fixed anoxic and aerobic reactor volumes, it is apparent that the recirculation ratio is an important operational parameter. Based on the results of the simulations presented in Figure 9, a recirculation ratio of three was initially selected for the pilot test run. However, influent NO<sub>3</sub>-N concentration increased prior to the start of the test run and a recirculation ratio of two was used.

Based on the SSSP simulations, the pilot plant was reconfigured to have an anoxic volume of 80 liters, an aerobic volume of 120 liters, and a recirculation ratio of two. Furthermore, the influent flow was reduced to 45 l/d. This change was made to provide an MLVSS concentration of 3,000 mg/l (4,500 mg/l as COD) based on updated COD load and yield data. After these changes were made, the system was operated for approximately 2 weeks prior to the start of the test run.

#### **Pilot Plant Test Run**

Pilot plant process parameters are summarized in Table 10. Average influent, anoxic reactor, and effluent characteristics are presented in Table 11. SSSP input and output for the actual test run conditions are presented in Figure 10. This simulation was run using the measured parameter values reported earlier.

#### **Organic Removal**

A COD balance around the system accounted for 98 percent of the influent COD, indicating that the data should be acceptable [9]. A plot of COD removed per unit biomass per unit time versus COD applied per unit biomass per unit time for the overall system during the pilot plant run is presented in Figure 11. The line of best fit indicates that 98.8 percent of the biodegradable COD was removed and no decrease in COD removal was observed at the highest loading rates. The intersection of the line of best fit with the x-axis represents a nonbiodegradable SCOD of 310 mg/l.

A chronological plot of effluent total BOD, SCBOD, NBOD, and BOD exerted by total suspended solids ( $BOD_{TSS}$ ) is pre-



FIGURE 12. Chronological plot of effluent total BOD, SCBOD, NBOD, and BOD of suspended solids.

sented in Figure 12. The plot and the effluent BOD data presented in Table 11 indicate that the majority (74 percent) of effluent total BOD was attributable to NBOD and BOD<sub>755</sub>. Because BOD<sub>755</sub> is a function of sludge settleability, which is inherently variable, tertiary filtration will be incorporated into the full-scale system. This will provide a greater margin of safety should effluent SCBOD or NBOD concentrations increase periodically in the full-scale system.

Effluent benzene and toluene were not analyzed during the test run because they were not detected in any of the analyses performed during startup. Effluent phenol concentrations were less than 0.01 mg/l during the test run. SSSP does not model removal of individual organic compounds.

#### Nitrogen Removal

A nitrogen balance around the system accounted for 91 percent of the influent total nitrogen. A plot of TKN removed per unit biomass per unit time versus TKN applied per unit biomass per unit time is presented in Figure 13. The plot indicates no decrease in removal at the highest TKN loading encountered. The intersection with the *x*-axis corresponds to a nonbiodegradable soluble TKN concentration of 28 mg/l. This value is equal to the average effluent concentration of 30 mg/l, less 2 mg/l nitrogen associated with effluent VSS.

Based on SSSP, the average effluent  $NH_3$ -N concentration was expected to be approximately 1 mg/l; however, 8 mg/l was obtained. To determine if growth-limiting conditions existed with respect to variables other than substrate and oxygen, a micronutrient analysis of the influent wastewater and biomass was performed at the midpoint of the test run. The analyses indicated that both the influent and biomass were deficient in calcium, magnesium, and potassium. The absence of these micronutrients may explain the incomplete nitrification. Although no additional pilot testing was performed to confirm this theory, provisions for addition of these micronutrients will be provided in the full-scale system. Assuming that the remaining 8 mg/l  $NH_3$ -N could have been removed,



FIGURE 13. TKN removed per unit biomass per unit time versus TKN applied per unit biomass per unit time.

	Anoxic Reactor		Aerobic Re	eactor	Overall System	
Parameter	Pilot Plant	SSSP	Pilot Plant	SSSP	Pilot Plant	SSSP
Total COD removed (g/d)	106	98	18	23	124	121
COD oxidized (g/d)	83ª	75	14	19	97	94
COD removed by cell synthesis	23ª	23	4	4	27	27
Nitrate consumed (g/d)	23	25	_	0.4	23	25
Nitrate consumed expressed as oxygen $(g/d)^b$	65	72	-	1.1	65	73
Oxygen consumed as oxygen (g/d)	0	0	63	72	63	72
Nitrogenous oxygen demand $(g/d)^c$	0	0	40	49	40	49
Carbonaceous oxygen demand $(g/d)^d$	65	72	23	23	88	95
Total oxygen demand (g/d)	65	72	63	72	128	144

2.86 mg O2/mg NO3-N

'Assumes 4.57 mg O2/mg NH3-N oxidized to nitrate

<sup>d</sup>Difference between oxygen consumed and nitrogenous oxygen demand

the actual nonbiodegradable TKN concentration would be 20 mg/l.

Oxidized nitrogen removal was directly related to daily COD loading. SSSP's prediction of oxidized nitrogen removal was nearly equal to pilot plant removal. Overall, the effluent  $NO_2/$  $NO_3$ -N concentration averaged 119 mg/l, while SSSP predicts 118 mg/l. In the anoxic reactor, the  $NO_2/NO_3$ -N concentration averaged 67 mg/l, while SSSP predicts 58 mg/l.

An alkalinity balance around the reactors indicates that 3.40 mg alkalinity/mg  $NO_3$ -N removed was recovered in the anoxic reactor and 7.29 mg alkalinity/mg  $NH_3$ -N converted to nitrate was consumed in the aerobic reactor. These values are very close to theoretical stoichiometric coefficients for alkalinity recovery and consumption. With respect to reactor alkalinity concentrations, SSSP predictions and actual concentrations were nearly equal. The anoxic and aerobic reactor alkalinity concentrations averaged 662 and 270 mg/l as CaCO<sub>3</sub>, respectively. SSSP predicted anoxic and aerobic reactor alkalinity concentrations of 675 and 255 mg/l, respectively, when expressed as CaCO<sub>3</sub>.

#### Sludge Production

The average MLVSS concentration in the anoxic and aerobic reactors was 2,466 and 2,519 mg/l, respectively. The measured COD/VSS ratio was 1.54 g COD/g VSS. Based on this ratio, SSSP predicted anoxic and aerobic reactor concentrations of 2,645 and 2,557 mg/l, respectively. These values represent very accurate predictions of sludge production. The net solids yield was 0.14 mg VSS/mg COD removed, and cell nitrogen content was 1.3 percent by weight. The mixed liquor VSS/TSS ratio was 0.89.

#### **Oxygen Requirements**

Table 12 presents a summary of oxygen requirements for each reactor, and compares these values with SSSP predictions. Again, actual and predicted values compare very well. A significant point to note is that the use of a single sludge system reduces the oxygen consumption by about half for this wastewater. This follows from the fact that the nitrate consumption, expressed as oxygen, is approximately equal to the oxygen consumption. If denitrification had not been employed, it would have been necessary to supply the total electron acceptor as oxygen.

#### CONCLUSIONS

Pilot test results indicate that DSM process wastewater can be treated to the required permit limits using a two-stage singlesludge carbon oxidation, nitrification, and denitrification process. The process was stable over a wide range of pollutant loadings and provided a reasonable level of safety for each permit parameter.

SSSP was a very useful tool for process design. Once calibrated for DSM wastewater, SSSP was used to evaluate many alternative process configurations in a relatively short time. The ability to experiment with various process parameters also enhances an engineer's understanding of the importance of these parameters with respect to system design. Although SSSP is a powerful modeling tool, it should be used by engineers as a guide to process design. Many factors influencing process



FIGURE 14. Full scale process flow diagram.

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design (microorganism inhibition, thermodynamic influences, priority pollutant removal, etc.) are not incorporated in the model and must be accounted for by the engineer.

SSSP predictions of anoxic and aerobic reactor MLVSS, COD, NH<sub>3</sub>-N, and NO<sub>3</sub>-N concentrations, sludge production, and oxygen and alkalinity requirements were very close to actual pilot plant values. These results indicate that the model can be calibrated with a reasonable degree of certainty by determining a few key wastewater and kinetic and stoichiometric parameters.

#### RECOMMENDATIONS

The recommended full-scale configuration showing major equipment sizes is presented in Figure 14. Fixed volume equalization was selected and sized to reduce the peak to average day oxygen demand ratio to approximately two. An anoxic selector was incorporated to control potential filamentous bacterial growth, although none was encountered in the pilot study. The distribution of anoxic to aerobic volume tested in the pilot study was altered slightly so that four equal-size tanks could be used (one equalization, one anoxic, two aerobic). A pumping capacity of up to three times the influent flow rate was selected for the recirculation system to provide flexibility. Centrifugal blowers and a coarse bubble diffuser system were selected for aeration. A pumping capacity of up to 1.5 times the influent flow rate was selected for the sludge recycle system.

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# Bioreactor Design Effects on Biodegradation Capabilities of VOCs in Wastewater

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Volatile organic chemicals are a wastewater pollution problem that can be handled by ultrafiltration, stripping, or biodegradation. Ultrafiltration and stripping transfer the dissolved organics to another phase which should then be further treated to finally destroy or utilize the organic chemicals. Biodegradation, on the other hand, converts the water soluble molecules to bio-molecules which can then be separated or directly discharged. Biodegradation of aromatic chemicals requires air and tests have conclusively shown that traditional biodegradation designs result in VOC stripping losses to the air stream rather than biodegradation.

Computer models and experimental data are presented comparing batch (plug flow), CSTR and packed bed bioreactor designs for their abilities to degrade VOC chemicals. Batch or plug flow reactors are shown to be a very poor method for biodegradation. CSTRs work well but require a large process residence time.

A new packed bed column bioreactor will be shown to provide much faster biodegradation and still minimize air stripping losses. Mass transfer and fluid mechanic parameters have been measured with and without biomass and compared to traditional chemical engineering correlations. The packed column minimizes the demand for air flow while increasing the throughput rate of wastewater as compared to a CSTR design. The efficiency of VOC biodegradation will be seen to be greatly improved.

#### INTRODUCTION

Organic chemicals dissolved in or physically associated with water are an important combination for the maintenance of life as we know it on this planet. Carbohydrates, fats and sugars (to name a few) are the everyday molecules that higher life forms have adapted as their major sources of energy and biological building blocks.

In relatively recent times, mankind has begun to extract and synthesize other forms of organic chemicals which have gained widespread use as fuels or fabrication materials. In accomplishing these goals, water is often a by-product which has

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#### **Table 1 Some EPA Priority Pollutants**

Benzene	
Carbon tetrachloride	
Chlorobenzene	
2-Chlorophenol	
1.2-Dichlorobenzene	
2.4-Dichlorophenol	
2.4-Dimethylphenol	
Methyl chloride	
Naphthalene	
2-Nitrophenol	
2.4-Dinitrophenol	
Phenol	
Pentachlorophenol	
Toluene	
Anthracene	
Trichlorethylene	
Vinyl chloride	
DDTs	
PCBs	
	Benzene Carbon tetrachloride Chlorobenzene 2-Chlorophenol 1,2-Dichlorophenol 2,4-Dimethylphenol Methyl chloride Naphthalene 2-Nitrophenol 2,4-Dinitrophenol Phenol Phenol Pentachlorophenol Toluene Anthracene Trichlorethylene Vinyl chloride DDTs PCBs

very little economic value and so must be disposed. Unfortunately, such water streams frequently contain quantities of dissolved organic chemicals which do not fall into the category of useful food sources for higher forms of life. In fact, many of these have been identified as harmful to nature or to life and the US EPA has identified several as priority pollutants due to their abundance or persistence in the environment. Table 1 shows a short list of a few of these priority pollutants.

In this paper, the biodegradation characteristics of toxic organic wastes in three liquid biotreatment facilities (the aerated lagoon (PFRs), well-mixed CSTRs and finally a packed bed bioreactor) are presented. The objective is to model the performance of these systems for their efficiency to biodegrade toxic pollutants and to observe air-stripping losses of volatile organics in each system. The Clean Air Act of the United States points out that the EPA estimates 2000 cancer cases are caused each year by just 17 airborne pollutants. Air-stripping of volatile wastes from water biodegradation systems is therefore a problem to be avoided. As such, each bioreactor is tested with three different VOC water pollutants: phenol, cresol and methyl ethyl ketone. Table 2 lists a few VOC air pollutants and diseases they cause.

The models will be seen to be fairly simplistic or "ideal" in several ways. However, it is not the purpose of this study, for instance, to be concerned about the behavior of a *real* aerated lagoon with toxic molecules being adsorbed and desorbed into lining materials, toxic chemical-consuming bacteria being themselves consumed by predators, poorly mixed regions in the lagoon, etc. In fact, it is one of the fundamental, philosophical beliefs of our group that chemical industries should be biodegrading their toxic water soluble wastes in "ideal"

#### Table 2 Air Pollutants and Associated Diseases

Phenol = 1. Respiratory Irritation				
2. Mutagenic				
Toluene = 1. Nervous System Depressed				
2. Carcinogen				
Trichlorethylene = 1. Cancer				
2. Nervous System Depressant				
Vinyl chloride = 1. Cancer				
Benzene = 1. Cancer (leukemia)				
Carbon tetrachloride = 1. Liver Cancer				
Cresol = 1. Skin Irritant				
2. Liver Damage				
Methyl chloride = 1. Cancer				
2. Nervous System Effects				

"ideal" vessels. Only in this manner can the biodegradation performance be optimized and uncontrolled releases of toxic chemicals to the environment prevented which otherwise seem to frequently result in environmental disasters in the future. Thus it is important to have a sound knowledge of the performance of pure process units for biodegradation of toxic water soluble wastes. This will lead to better designs of biodegradation facilities.

Finally, the models described are both theoretical and experimental with the goal being in every case to closely link the predictions of the simplest theoretical model to the behavior of the ideal experimental system.

#### THEORETICAL EQUATIONS

#### **Biogrowth Equation**

In all bioreactors, it is assumed a pure culture of bacteria is consuming the toxic molecules according to Haldane's [1] non-structured, inhibition model:

$$\frac{dX}{dt_{growth}} = \frac{\mu_m S}{K_s + S + S^2/K_I} * X \tag{1}$$

The change or loss of substrate due to growth is identical to this but divided by the biomass yield coefficient,  $Y_x$  which, is assumed constant.

#### **Equilibrium Condition**

The dissolved organic compound is assumed to have an equilibrium concentration between the liquid and air phase given by Henry's constant:

$$y = HS_I^*/(RT) \tag{2}$$

#### Batch Bioreactor (Plug Flow, Aerated Lagoon)

It is possible to correlate the results of an ideal batch bioreactor directly to an ideal plug flow bioreactor just by changing time in the former case to residence time in the latter. Thus numbers generated from experimental batch studies can imply conditions in an aerated lagoon.

In the theoretical model, the reasoning of MacKay *et al.* [2], is used such that both the air and liquid phases are well mixed. The air phase is flowing steadily and leaving the bioreactor with toxic molecules in equilibrium with the bulk liquid phase. The resulting dynamic equation in terms of the organic concentration in the liquid phase is:

$$\frac{dS}{dt} = \frac{-\mu_m SX}{Y_x (K_s + S + S^2/K_l)} - \frac{HQ}{VRT} S$$
(3)

Solution is straightforward by numerical integration techniques.

#### Continuous, Well Mixed Bioreactors

A series of well mixed tanks is hypothesized in which the liquid phase flows in a series fashion from the first to the last tank while the air phase is allowed to flow either countercurrent or cross-current through the bioreactors. The design study is carried out in this manner for three major reasons: (1) recent work has shown series bioreactors can greatly enhance waste treatment rates (Hill and Robinson [3]), (2) existing aerated lagoons could be seen as dispersed plug flow for which series bioreactors can be used to model and (3) in practice multiple "toxins" could be treated with different ecosystems in each bioreactor. Again it is assumed the air phase is in equilibrium in all bioreactors but this time three algebraic equations need to be solved simultaneously for each bioreactor:

$$F(S_{i-1} - S_i) = Q(y_i - y_{i+1}) + \frac{\mu_m S_i X_i V_i}{Y_x (K_s + S_i + S_i^2 / K_I)}$$
(4)

$$F(X_i - X_{i-1}) = \frac{\mu_m S_i X_i V_i}{K_s + S_i + S_i^2 / K_I}$$
(5)

$$y_i = HS_i / (RT) \tag{2}$$

Solution of these series, non-linear algebraic equations is made difficult by known boundary conditions existing at either end of the bioreactor train for counter-current air flow. A rather unique "guessing" numerical procedure was developed to overcome this problem.

#### Packed Column Bioreactor

The final ideal bioreactor is the common packed bed or packed column design. This design was chosen to enhance biodegradation rates without requiring recycle. By holding up a high density slime layer of microorganisms on an inert packing, the packed column approaches that of a high cell recycle bioreactor. The column must be packed and not fluidized because collision between particles is a severe detriment to the mechanical stability of the slime layer. The column is assumed to be at steady state but conditions vary down the length of the column. The differential equations expressing these conditions are:

$$D_{z}\phi_{L}\frac{d^{2}S}{dz^{2}} - F/A\frac{dS}{dz} - K_{L}a(S - S_{I}^{*})\phi_{L} - \frac{\mu_{m}SX_{T}\phi_{L}}{Y_{x}(K_{s} + S + S^{2}/K_{I})} = 0 \quad (6)$$

$$D_{z}\phi_{L}\frac{d^{2}X}{dz^{2}} - F/A\frac{dX}{dz} + \frac{\mu_{m}SX_{T}\phi_{L}}{K_{s} + S + S^{2}/K_{I}} = 0$$
(7)

$$-Q/A \frac{dy}{dz} + K_L a (S - S_I^*) \phi_L = 0$$
 (8)

The above non-linear differential equations must be solved simultaneously advancing from the top (z=0 liquid phase inlet)to the bottom (z=L liquid phase outlet) of the bioreactor. However, they contain fluid mechanics and mass transfer parameters which also need to be simultaneously computed. This equation is:

$$\tau = \alpha_1 (F/A)^{\alpha 2} (Q/A)^{\alpha 3} \tag{9}$$

where  $\tau$  is either liquid holdup,  $\phi_L$ , dispersion,  $D_z$ ; or mass transfer coefficient,  $K_L a$ . The  $\alpha$  constants in equation 9 can be extracted from empirical correlations in the literature but preferably come from "best-fitting experiments" performed on the experimental or industrial apparatus being used. The latter case was used in this work.

Also of critical importance in this bioreactor are the characteristics of the biomass. For modeling purposes, we assume the biomass is either in the free form (X, suspended in the $liquid) or in the slime layer <math>(X_F)$  giving a total biomass concentration  $(X_T)$ . The slime layer contribution can be computed once the slime layer thickness  $(\delta_F)$  is known from:

$$X_F = 2\delta_F / (d_p \phi_L) \tag{10}$$

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Solutions of equations 6 to 10 require five boundary conditions. The liquid phase organic, air phase organic and liquid phase biomass concentrations coming into the bioreactor are known and the last boundary condition is stated mathematically as:

$$dS/dz = dX/dz = 0$$
 at  $z = L$  (11)

Equation 11 states there is no diffusive flux of organic molecules or microorganisms out of the bioreactor into the exiting stream. These simultaneous differential and algebraic equations are very difficult to solve since they are highly nonlinear and involve boundary conditions at opposite ends of the bioreactor. No commercial software was found which was successful in handling this system so a unique sequential numerical algorithm was developed. However, it will also not be discussed here.

#### **EXPERIMENTAL**

Batch studies were performed in both a well mixed, temperature controlled Erlenmeyer flask and the New Brunswick BioFlo I fermentor. Continuous runs were performed in the New Brunswick BioFlo I while the packed column bioreactor was fabricated locally and is sketched in Figure 1.

In all biodegradation experiments, the microorganism used was Pseudomonas putida. McKinney's modified medium was used as the mineral source (Hill and Robinson [4]) while phenol, cresol and catechol were used as the organic waste molecules. The concentration of biomass was determined by optical density measurements on a spectrophotometer at 600 nm. The concentration of organic molecules was determined on a UV spectrophotometer at 273 nm. Both curves were pre-calibrated. Biomass samples were diluted to fall below an optical density of 0.45 while organic samples were filtered and diluted to fall below a concentration of 10 ppm. In addition, for the packed column, liquid holdup was determined by measuring excess fluid after suddenly stopping flows. Dispersion was evaluated by injecting an impulse concentration of salt and measuring outlet concentrations. Finally, the mass transfer coefficient was evaluated by conducting pure stripping experiments and measuring phenol and cresol in the effluents.



FIGURE 1. Sketch of packed column bioreactor



FIGURE 2. Volatility effects on air stripping losses

#### **RESULTS AND DISCUSSION**

#### **Batch Bioreactor**

The fact that phenol molecules are stripped by air from wellmixed bioreactors in a logarithmic fashion has been clearly shown [5]. This behavior of the dissolved phenol concentration in the broth when no biogrowth is occurring in the batch reactor upholds MacKay's equilibrium theory and gives a best fit value to Henry's Law coefficient for phenol of 7.2\*10<sup>-7</sup> atm m<sup>3</sup>/gmole. This value is very close to accepted literature values for the Henry's Law coefficient of phenol. Varying the Henry's Law value in the batch growth theoretical equations allows one to predict what will happen in a batch (or plug flow) bioreactor with different volatility chemicals. Figure 2 shows three curves using typical biogrowth kinetics for toxic organic molecules. The outer curve corresponds to no stripping (H = 0), the middle curve corresponds to cresol while the inner curve is for the high volatility chemical MEK. It can be clearly seen that even with cresol, significant losses of chemical are oc-



FIGURE 4. Degradation and stripping predictions of phenol in series CST bioreactors

curring to the air phase in a batch reactor while for MEK, the majority of change is due to air stripping, not biodegradation.

This model also fits correctly into batch biogrowth data with phenol as shown in Figures 3. In short, the air stripping causes the complete initial decline in phenol concentrations particularly at high initial concentrations when growth is severely inhibited. Over a 50 hour time period, the phenol drops from 476 ppm to 360 ppm or by about 25% due solely to air stripping. The crucial point is this, aerated lagoons which act like plug flow bioreactors will follow the same pattern such that 25% of the phenolics will be lost to the air in the initial half of the lagoon system. This conclusion is supported by the abundant new data in the literature reporting high volatile organic concentrations in the air surrounding industrial waste lagoons.

#### **Continuous Well-Mixed Bioreactors**

The other extreme of the batch or plug flow bioreactor is the traditional continuous well-mixed bioreactor. Here, not only is sufficient mixing provided to ensure the contents of the bioreactor are homogeneous, but also a steady state is



FIGURE 3. Batch bioreactor performance at So = 476



FIGURE 5. Experimental CST bioreactor data with phenol

achieved by continuously pumping fresh feed and removing an equal mass of bioreactor fluid.

The theoretical calculations associated with this system of bioreactors for stripping and biodegradation (solutions of equations 2, 4, and 5) show that counter-current air flow extracts or strips a larger portion of organic molecules than crosscurrent air flow. This is a well-known mass transfer phenomenon. The conclusion being that in order to reduce air stripping loss, well-mixed bioreactors should utilize a cross-current air flow pattern. Figure 4 then shows the predicted liquid phase and air phase concentrations in a series of 4 cross-current, wellmixed bioreactors degrading phenol. The point to observe is that although phenol is lost out of the liquid phase only a very small quantity gets into the air phase. The majority of this loss to the air stream occurs only in the first bioreactor and only at a concentration of less than  $6 * 10^{-7}$  g/L. Recalling that the batch or plug flow reactor gave 25% stripping with phenol, the well-mixed bioreactor yields a much lower loss of only 0.001%. The experimental data from the New Brunswick Bioflow fermentor confirmed these predictions as shown in Figure 5. Up to a dilution of 0.34 h<sup>-1</sup>, the biomass level remained constant and high while the phenol concentration in the liquid phase is constant and very low (ppb here) and no phenol was detected in condensate samples taken from the air exhaust stream.

These theoretical calculations supported by the experimental data have clearly shown that the well-mixed bioreactor is capable of complete phenol degradation with very low losses to the atmosphere. This would tend to favor this design for waste treatment systems but even the well-mixed bioreactor has a severe problem. The rate at which this biodegradation occurs is very low with typical maximum values of only  $1.0*10^{-5}$  kg/m<sup>3</sup>-s being reported. Thus large well-mixed vessels would be required for industrial applications leading to a fairly significant capital investment. A 5000 m<sup>3</sup> per hour discharge requires well-mixed vessels totalling 20000 m<sup>3</sup> and extensive operating expenses to keep the liquid phase well-mixed and aerated.

#### **Packed Column Bioreactor**

In an effort to overcome this last problem, a new bioreactor configuration (albeit common chemical reactor configuration) has been investigated. The packed column bioreactor is an attempt to increase the reaction rate by maintaining a high concentration of biocatalyst (i.e., the microorganisms) inside the bioreactor. *Pseudomonas putida* excrete a sticky polysaccharide substance which allows them to adhere to solid surfaces. A slime layer of 100 to 200 microns is developed and previous workers have found that this film is "congested"

Before theoretical predictions could be made, the fluid mechanics ( $\phi_L$  and  $D_z$ ) and mass transfer ( $K_L a$ ) functions were empirically fit to equation 9 using the experimental procedures described earlier. The values of the best-fit parameters determined for the experimental packed column were:

$$\phi_L$$
:  $\alpha_1 = 13.08$ ;  $\alpha_2 = 0.69$ ;  $\alpha_3 = 0.17$   
 $D_z(m^2/s)$ :  $\alpha_1 = 5.14$ ;  $\alpha_2 = 1.33$ ;  $\alpha_3 = 0.00$   
 $K_L a(h^{-1})$ :  $\alpha_1 = 0.293$ ;  $\alpha_2 = 0.74$ ;  $\alpha_3 = 0.89$ 

All parameters are valid over the ranges:

$$3 * 10^{-5} < F/A < 20 * 10^{-5} m/s$$
  
 $1 * 10^{-3} < Q/A < 11 * 10^{-3} m/s$ 

The liquid holdup was found to be significantly increased (by



FIGURE 6. Packed column liquid hold-up vs theory of Otake and Okada

a factor of 3.2) once a biofilm developed on the glass beads. The dispersion coefficient was not affected by the biofilm. The experimental verification of these parameters as compared to literature correlations for these fluid mechanics and mass transfer functions are shown in Figures 6 to 8. Figure 6 indicates that the correlation of Otake and Okada [6] gave liquid holdups which were frequently of lower value than we measured or correlated. Figure 7 shows the dispersion coefficient correlation of Sater and Levenspiel [7] was consistently shifted up about 5 m<sup>2</sup>/s from the experimental measurements. Figure 8 shows that the best fit correlation developed here reasonably predicted the observed trends in air stripping while the correlation of Goto and Smith [8] predicted much smaller amounts of stripping. The point of all this is that it is very necessary to measure and correlate how a column is actually performing rather than using general correlations, which can be different by an order of magnitude. Use of incorrect functions in a bioreactor model will yield correspondingly incorrect interpretations of the biokinetics of the reactor and thus make design calculations erroneous.







FIGURE 8. Mass transfer characteristics of the packed column

The final but probably most important results to be discussed is the biodegradation performance of the packed column bioreactor. The solution of the theoretical model (equations 6 to 11) led to the design used in the experiment. For instance, initially a simulation was performed to predict the performance of the column bioreactor without any biofilm growth  $(X_F = 0)$ . The biokinetic parameters used in this analysis came from earlier work (Hill and Robinson [4]). Obviously in this case, a continuous inoculum of microbes is required in the feed since microbes will otherwise be quickly washed out. The column is behaving essentially like a dispersed/plug flow reactor. At reasonable inoculums of 0.5 to 5.0 gDW/L, it was discovered that there is next to zero biodegradation in the short residence time of a 0.25 meter long column. Significant biodegradation occurs only when unreasonably large inoculums are used making the design concept rather useless unless a biofilm is developed. On the other hand, Figure 9 shows the predicted biodegradation effect of a biofilm in both a 0.25 m and 1.25 m column. The top three curves indicate that the short column starts to become effective when a thick biofilm of 200 microns coats the packing, but by adjusting the column length to 1.25 m, the thick biofilm causes a very significant drop in phenol



FIGURE 9. Predicted biofilm performance of the packed column bioreactor



FIGURE 10. Packing diameter effects on predicted performance of the packed column bioreactor

concentration. The packing size used in all the above studies was 5 mm.

Figure 10 shows what occurs when the packing diameter of the column is changed. As the diameter of the packing drops to 2.5 mm from 5.0 mm, almost complete biodegradation occurs. However, there is a price to be paid for this improvement. Smaller packing begins to quickly reduce the flux of wastewater which can be easily pumped through this three phase reactor. It also greatly enhances the chances of plugging due to microbial floc build-up or small particles in the wastewater. For these conflicting reasons, the experimental study was conducted using 3 mm glass beads.

The experimental results first of all clearly showed that air flux had no effect on biodegradation over the range of 0.001m/s to 0.011 m/s. The effluent water was always completely saturated with oxygen and the phenol biodegradation results were not changed by varying air flowrate. However, if the aeration rate was stopped, biodegradation ceased. These results indicate that there is a critical low air flux which will reduce biodegradation, but at the liquid fluxes and organic loadings used in this study, it was well below the value 0.001 m/s. The bioreactor should be operated at low air flux as this increases the void space available to liquid flow.



FIGURE 11. Biodegradation results with phenol in the packed column

In operation, the column takes on a deep green color when the full biofilm is developed after about 6 days in the batch mode followed by 4 days in a continuous start-up mode. After operation for about 9 weeks, the beads were removed and were found to be remarkably uniformly coated with biofilm. The average biomass per bead was measured at 0.62 mg DW, and assuming an approximate dryweight percentage of 15 and an approximate wet weight density of 1000 kg/m<sup>3</sup>, the biofilm thickness was calculated to be about 200 microns.

Figure 11 shows the experimental biodegradation data for phenol in the column. The circular markers represent the % degradation of the phenol in the 1.25 meter column at different liquid flow rates. The feed concentration was 500 ppm for all those data points. The line on this graph is the predicted % degradation from the solution of equations 6 to 11 using the experimental correlation parameters just described, the biokinetics reported in the previous paper (Hill and Robinson [4]) and a biofilm depth of 200 microns. The agreement is extremely good giving a strong indication that the model is quite adequate for describing the behavior of this substrate inhibited, packed bed bioreactor.

The amount of air stripping from the packed bed bioreactor was also very small. When 100% biodegradation was achieved, phenol could not be detected in air-condensate samples. At 33% biodegradation, only 0.07% of all the phenol fed to the bioreactor was detected in the airstream. The rest of the nondegraded phenol left in the liquid effluent line.

#### CONCLUSIONS

Wastewater biodegradation facilities treating toxic organic chemicals should not be operated in the batch or plug flow operating modes. These designs lead to large losses of organic molecules due to air-stripping even for low to medium volatility chemicals such as phenol. At 500 ppm concentration, 25% of the phenol molecules were lost from batch bioreactors due to air-stripping. Continuous well-mixed bioreactors were found to completely degrade phenolics up to a dilution rate of 0.3  $h^{-1}$ . No air-stripping losses were observed in condensate samples taken from the continuous bioreactors. However, these designs suffer from low processing rates requiring extremely large bioreactors.

Both the above observations were modeled successfully on the computer involving the solution of a non-linear ordinary differential equation for the batch (plug flow) bioreactor and a series of non-linear algebraic equations for the continuous bioreactors. These computations permitted design strategies to be tested and it was found for instance, that cross-current air flow in series, continuous bioreactors reduces air-stripping losses as compared to countercurrent air flow. A model was also developed for a packed bed "slime" reactor which involved solving three simultaneous non-linear ordinary differential equations with five boundary conditions. This model predicted that such a bioreactor could be designed to efficiently degrade phenols with little air-stripping losses.

Experimental data with the packed bed bioreactor was used to generate parameters for liquid hold-up, dispersion and mass transfer. Biodegradation studies with the bioreactor showed that a uniform, 200 micron biofilm was developed on the packing and confirmed the theoretical model predictions for phenol biodegradation. Phenol was successfully treated at processing rates up to  $10^{-4}$  kg/m<sup>3</sup>-s, well above the maximum rates normally achieved with aerated lagoons or even continuous, well-mixed bioreactors.

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#### NOTATION

- $A = \text{column cross sectional area, } m^2$
- $d_n = packing diameter, m$
- $D_z$  = dispersion coef., m<sup>2</sup> s<sup>-1</sup>
- F = liquid flowrate, m<sup>3</sup> s<sup>-1</sup>
- H = Henry's constant, atm m<sup>3</sup> gmole<sup>-1</sup>
- $K_I$  = inhibition growth constant, kg m<sup>-3</sup>
- $Q = air flowrate, m^3 s^{-1}$
- $K_L a = \text{mass transfer coef. s}^{-1}$ 
  - $R = \text{gas constant}, \text{ atm } \text{m}^3 \text{ gmole}^{-1} \text{ }^\circ\text{K}^{-1}$
  - S = substrate concentration, kg m<sup>-3</sup>
- $S_I^*$  = interfacial substrate concentration, kg m<sup>-3</sup>
- t = time, s
- $T = \text{temperature}, ^{\circ}\text{K}$
- V = bioreactor liquid volume, m<sup>3</sup>
- X = biomass concentration, kg DW m<sup>-3</sup>
- y = substrate concentration in air, kg m<sup>-3</sup>  $Y_x =$  biomass yield coef., kg DW kg<sup>-1</sup>
- z = distance, m

#### Greek

- $\alpha$  = parameter in eq 9
- $\mu$  = specific growth rate, s<sup>-1</sup>
- $\mu_m$  = maximum specific growth rate, s<sup>-1</sup>
- $\delta_F$  = biofilm thickness, m
- $\phi_l =$ liquid holdup

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# **New Storm Water Regulations Impact Industry**

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In November 1990, new Environmental Protection Agency (EPA) regulations aimed at governing the discharge of storm water from industrial facilities became effective. Because some industrial runoff contains toxics and other pollutants, the EPA considers storm water a major source of water contamination. The new regulations will have a profound impact on the National Pollutant Discharge Elimination System (NPDES) permit requirements for industry. This paper summarizes the new storm water regulations, focusing on the requirements for industrial facilities. It also presents suggestions for compliance.

#### INTRODUCTION

The storm water regulations have been under development for approximately 10 years. The agency's efforts to regulate the many diverse sources of storm water pollution have been extremely controversial. A draft rule was published in the *Federal Register* on December 7, 1988. After several delays, the final regulations were signed by EPA Administrator, William Reilly, on October 31, 1990. They were published in the *Federal Register* on November 16, 1990. Extensions and proposed extensions for some of the permit application deadlines were published in the *Federal Register* on March 21, 1991.

#### **Affected Industries**

Under the new regulation, any facility that discharges storm water associated with industrial activity will be required to obtain an NPDES storm water permit. The rule applies both to facilities that discharge directly into waters of the United States and those that discharge to municipal or private storm water sewer systems. The following categories of facilities are considered to be engaged in "industrial activities:"

- Facilities subject to storm water effluent limitation guidelines, new source performance standards, or toxic pollutant effluent standards under 40 CFR Subchapter N (except facilities with toxic pollutant effluent standards that are exempted under Category 11, below).
- Facilities classified as SIC 24 (except 2434); 26 (except 265 and 267); 28 (except 283); 29; 311; 32 (except 323); 33; 3341; 373 (including lumber; paper; chemical; petroleum; leather tanning and finishing; stone, clay, glass and

concrete; smelting, refining, and manufacture of related metal products; and ship building and repairing).

- 3. Facilities classified as SIC 10 through 14 (including active or inactive mining operations, except for areas of coal mining operations no longer meeting the definition of a reclamation area), and oil and gas exploration, production, processing or treatment operations, or transmission facilities that discharge storm water contaminated by contact with or that has come into contact with overburden, raw material, products, or wastes.
- Hazardous waste treatment, storage, or disposal facilities, including those that are operating under interim status or a permit under Subtitle C of RCRA.
- Landfills, land application sites, and open dumps that receive or have received any industrial wastes, including those that are subject to regulation under Subtitle D of RCRA.
- Facilities involved in recycling of materials, including metal scrapyards, battery reclaimers, salvage yards, and automobile junkyards, including, but not limited to, SIC 5015 and 5093.
- Steam electric power-generating facilities, including coal handling sites.
- 8. Transportation facilities classified as SIC 40, 41, 42 (except 4221-25), 43, 44, 45, and 5171, which have vehicle maintenance shops, equipment cleaning operations, or airport deicing operations. Only those portions of the facility that are either involved in vehicle maintenance (including vehicle rehabilitation, mechanical repairs, painting, fueling, and lubrication), equipment cleaning operations, or which are otherwise identified as associated with industrial activities.

- 9. Treatment works treating domestic sewage, or any other sewage sludge or wastewater treatment device or system storing, treating, recycling, or reclaiming municipal or domestic sewage with a design of 1.0 mgd or more, or required to have an approved pretreatment program under 40 CFR 403 (does not include off-site sludge management lands where sludge is beneficially reused or areas in compliance with Section 405 of the CWA).
- 10. Construction activities, including clearing, grading, and excavation activities, except operations that result in the disturbance of less than 5 acres, which are not part of a larger common plan of development or sale.
- 11. Facilities under SIC 20, 21, 22, 23, 2434, 25, 265, 27, 283, 285, 30, 31 (except 311), 323, 34 (except 3441), 35, 36, 37 (except 373), 38, 39, and 4221-25 (including food; tobacco; textile; apparel; wood kitchen cabinets; furniture; paper/paperboard products; printing; drugs; paints; varnishes, lacquers and enamels; rubber and plastics; leather; glass products made of purchased glass; fabricated metal products; industrial and commercial machinery and computer equipment; electronic equipment; transportation equipment; measuring, analyzing, and controlling instruments and photographic, medical, and optical goods, and watches and clocks; manufacture of miscellaneous items, such as jewelry, silverware, and musical instruments, among others; and certain warehousing and storage manufacturers). For this particular class of facilities, only those manufacturing, processing, or material storage areas that are exposed to storm water are considered to contribute "storm water associated with industrial facilities." Areas located on plant lands separate from the plant's industrial activities, such as office buildings and accompanying parking lots, are not considered "storm water associated with industrial activities" as long as the drainage from the excluded areas is not mixed with storm water that is associated with industrial activities.

Except as clarified under Paragraph 11, above, the term "storm water runoff associated with industrial activities" includes, but is not limited to:

- Storm water discharges from industrial plant yards
- Immediate access roads and rail lines used or traveled by carriers of raw materials, manufactured products, waste material, or by-products used or created by the facility
- Material handling sites
- Refuse sites
- Sites used for the application or disposal of process waste waters
- Sites used for the storage and maintenance of material handling equipment
- · Sites used for residual treatment storage or disposal
- Shipping and receiving areas
- Manufacturing buildings
- Storage areas (including tank farms) for raw materials, and intermediate and finished products
- Areas where industrial activity has taken place in the past, and where significant materials remain and are exposed to storm water

The regulation also affects large municipal storm sewer systems (serving populations greater than 250,000) and medium municipal storm sewer systems (serving populations greater than 100,000, but less than 250,000). The EPA estimates that approximately 100,000 industrial facilities, 173 cities, and 47 counties will be impacted.

#### BACKGROUND

The 1972 amendments to the Federal Water Pollution Control Act (referred to as the Clean Water Act or CWA) prohibits discharge of any pollutant to navigable waters from a point

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source unless the discharge is authorized by an NPDES permit. This legislation provides a means to control pollutants in point source discharges.

A number of studies conducted during the last 10 years concluded that diffuse sources of water pollution are a leading cause of water quality impairment. Studies have shown that storm water from residential and commercial areas can contain a variety of pollutants, including heavy metals, fecal coliform, pesticides, suspended solids, and nutrients. Runoff from industrial facilities can contain additional pollutants, depending on the nature of industrial activities, and the material management and waste disposal practices. Other studies have shown that many storm sewers also receive illicit discharges of untreated nonstorm water, spills, and large amounts of improperly disposed wastes, particularly used oils.

The Water Quality Act (WQA), passed in 1987, contains provisions that specifically address storm water discharges. The WQA requires the EPA to promulgate final regulations governing storm water permit applications for storm water discharges associated with industrial activity and discharges from large municipal separate storm sewer systems (serving populations of 250,000 or more) no later than February 4, 1989. In addition, the EPA is required to promulgate final regulations governing storm water permit application requirements for discharges from medium municipal separate storm sewer systems (serving populations of 100,000 or more, but less than 250,000) no later than February 4, 1991.

On December 7, 1988, Draft Storm Water Regulations were published in the Federal Register. The proposed regulations required permit applications for discharge of storm water from industrial facilities into waters of the United States, as well as from medium and large municipal separate storm water systems.

On April 20, 1989, the EPA was served notice of intent to sue by Kathy Williams et al., because of the Agency's failure to promulgate final storm water regulations on February 4, 1989, as required by the WQA. A suit was filed on July 20, 1989. On October 20, 1989, the EPA entered into a consent degree, agreeing to promulgate final regulations no later than July 20, 1990. The consent decree was later amended to provide for a promulgation date of October 31, 1990.

#### **OPTIONS FOR INDUSTRY**

The final rule provides three different options for industry:

- General permits
- · Individual permits
- Group permits

#### **General Permits**

A key to the EPA's strategy, as set forth in the final regulation, is the general permit. With the general permit option, the EPA intends to establish a framework developing permitting priorities. The preliminary strategy includes a four-tier set of priorities for issuing permits to be implemented over time. Where possible to implement this tiered approach, the EPA hopes to minimize the permitting effort both for industry and for the permitting agency.

- Tier I—Baseline Permitting. One or more general permits will be developed to initially cover the majority of storm water discharges associated with industry activity.
- Tier II—Watershed Permitting. Facilities within watersheds shown to be adversely impacted by storm water discharges associated with industrial activity will be targeted for permitting.
- Tier III—Industry-Specific Permitting. Special industry categories will be targeted for individual or industry-specific permits.

 Tier IV—Facility-Specific Permitting. A variety of factors will be used to target specific facilities for individual permits.

The EPA intends to use the general permit approach to initially cover the majority of storm water discharges associated with industrial activity in states without authorized NPDES programs. The EPA is encouraging states that do have NPDES permitting authority to use a similar approach.

Industries that are able to, and choose to be, covered under a general permit may submit a Notice of Intent (NOI) to be covered by the general permit. The requirements for submitting NOIs are not established in the final rule, but will be specified by the permitting agency. The EPA will be providing further guidance about the four-tier permitting strategy in general and specifics of the general permits in the next few months.

#### **Individual Permits**

Industrial facilities that are not allowed to or do not wish to be covered under the general permit, may apply for an individual permit. Applicants for discharges composed entirely of storm water are required to submit Form 1 and Form 2F. Applicants for discharges composed of storm water and nonstorm water was required to submit Form 1, Form 2C, and Form 2F. Applicants for new sources or new discharges composed of storm water and nonstorm water are required to submit Form 1, Form 2D, and Form 2F.

The submittal must also include the following:

- A site map showing:
  - Topography (if available)
  - All drainage and discharge structures
  - The drainage area of each storm water outfall
  - Paved area and buildings within the drainage area of each storm water outfall; past or present areas used for outdoor storage or disposal of significant materials; existing structural control measures to reduce pollutants in storm water runoff, material loading, and access areas; and areas where pesticides, herbicides, soil conditioners, and fertilizers are applied.
  - Hazardous waste treatment, storage, or disposal facilities
  - Wells where fluids from the facility are injected underground
  - Springs and other surface water bodies that receive storm water discharges from the facility
- An estimate of the area of impervious surfaces and the total area drained by each outfall (within a mile radius of the facility) and a narrative description of the following:
  - Significant materials that, in the 3 years prior to the submittal of this application, have been treated, stored, or disposed in a manner to allow exposure to storm water
  - Method of treatment, storage, or disposal of such materials
  - Materials management practices employed in the 3 years prior to the submittal of this application to minimize contact by these materials with storm water runoff
  - The location, manner, and frequency in which pesticides, herbicides, soil conditioners, and fertilizers are applied
  - The location and description of existing structural and nonstructural control measures to reduce pollutants in storm water runoff
  - A description of the treatment the storm water receives, including the ultimate disposal of any solid or fluid wastes other than by discharge
- A certification that all outfalls that should contain storm water discharges associated with industrial activity have been tested or evaluated for the presence of nonstorm water discharges that are not covered by an NPDES permit; tests for such nonstorm water discharges may include smoke tests, fluorometric dye tests, and analysis of accurate schematics.

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The certification must include a description of the method used, the date of any testing, and the onsite drainage points that were directly observed during a test

- Existing information regarding significant leaks or spills of toxic or hazardous pollutants at the facility that have taken place within the 3 years prior to the submittal of the application
- Quantitative data based on storm water sampling from all outfalls containing a storm water discharge associated with industrial activity for the following parameters:
  - Any pollutant limited in an effluent guideline to which the facility is subject
  - Any pollutant listed in the facility's NPDES permit for its process wastewater
  - Oil and grease, pH, BOD5, COD, TSS, total phosphorous, total Kjeldahl nitrogen, and nitrate plus nitrite nitrogen
  - Certain other conventional, nonconventional, toxic, or hazardous pollutants expected or known to be in the discharge [per 40 CFR 122.21 (g) 7 (iii) and (iv)]
  - Flow measurements or estimates of the flow rate and total amount of discharge for the storm event sampled, and the method of flow measurement or estimation
  - The date and duration or the storm event sampled, rainfall measurements or estimates of the storm event which generated the sampled runoff, and the duration between the storm event sampled and the end of the previous measurable (>0.1 inch of rainfall) storm event

#### **Group Permits**

Industrial facilities that are part of the same subcategory, or are sufficiently similar, may apply for a group permit in lieu of the individual or general permit. The group permit is comprised of two parts:

• Part 1 of the group application must be submitted to the EPA (Office of Water Enforcement and Permits, U.S. EPA located at 401 M Street, S.W., Washington, D.C. 20460 [EN-336]) for approval. Part 1 of the group application must:

- Identify the participants in the group application by name and location, listing the participants in nine subdivisions based on the facility location relative to the nine precipitation zones
- Include a narrative description summarizing the industrial activities of the participants and explaining why the participants are sufficiently similar to be covered by a general permit.
- Include a list of significant materials stored that are exposed to precipitation by participants in the group application and materials management practices employed to reduce contact by these materials with precipitation and storm water runoff
- Identify 10% of the dischargers in the group application for which quantitative data will be submitted (with a minimum of 10 discharges and either a minimum of two dischargers from each precipitation zone in which 10 or more members of the group are located, or one discharger from each precipitation zone in which nine or fewer members of the group are located; if more than 1,000 facilities are identified in the group application, no more than 100 dischargers must submit quantitative data; for groups between four and ten discharges, at least half of the facilities must submit quantitative data and at least one facility in each precipitation zone in which members are located must submit data). A discussion must be included, describing why the facilities selected to perform sampling and analysis are representative of the group as a whole. Different factors impacting the nature of the storm water dischargers, such as the processes used and material management practices, shall be represented to the extent feasible in

a manner roughly equivalent to their proportion in the group.

 Part 2 must contain quantitative data (NPDES Form 2F), as described above, for the individual permit, so that when Part 1 and Part 2 of the group application are taken together, a complete NPDES application (Form 1, Form 2C, and Form 2F) can be evaluated for each of the facilities selected for sampling.

#### Notification to Municipal Systems

Any operator of a facility that discharges storm water associated with industry activity through a municipal system serving a population of more than 100,000 people is required to submit notification of the discharge to the operator of that municipal system. The notification must include the name of the facility; the name and phone number of a contact person; the location of the discharge; a description, including SIC, which describes the principal products or services provided by the facility; and any existing NPDES permit number.

#### **REGULATORY DEADLINES**

#### **General Permit**

Deadlines have not yet been established for submitting a NOI to be covered under the general storm water permit. More information is expected to be provided on this option in the coming months.

#### **Individual Permit**

The deadline for submitting an individual permit application is currently November 18, 1991. EPA has proposed extending the individual permit application deadline to May 18, 1992 (published in the Federal Register on March 21, 1991, pg. 12101-12102). It is uncertain at this time whether the extension will be implemented.

#### **Group Permits**

The application deadlines for the group permits have been extended (published in the Federal Register on March 21, 1991, pg. 12098-12100). Part 1 of the group permit application must be submitted by September 30, 1991. Part 2 of the group permit application must be submitted to EPA by May 18, 1992.

#### Notification to Municipal Systems

Any industry required to notify the operator of their municipal storm sewer system is required to do so no later than 180 days after November 16, 1990 (the publication date of the final rule).

#### ADDITIONAL DIRECTIONS AND GUIDELINES

Some additional information is expected from the EPA that should help industries evaluate the permitting options available to them. First, the EPA is expected to publish an implementation rule which will outline the Agency's strategy, with particular focus on the four-tier approach and the role of the general permits in this strategy. A proposed general permit is expected to be included. Changes to the storm water discharge monitoring requirements may be included as well. The implementation rule is expected to be published in draft form in the next few months.

The EPA is also in the process of developing two guidance manuals. The first manual (or set of manuals) will be written to assist industries and municipalities that are preparing permit applications. The second manual will provide guidelines for agencies responsible for writing and approving permits.

#### **HOW TO COMPLY**

The first step in complying with these complex regulations is to determine whether your facility will be required to obtain a permit for storm water discharges. A careful review of the regulation, particularly Section 122.26 a (1) and (14), should help answer this question.

If it appears that your facility will be required to obtain a storm water permit, you will need to decide which options are available and will best suit your needs. Since the general permit option is not well defined at this time, it will be important to stay informed. Contact your local NPDES permitting agency or the EPA directly. Three names are listed in the regulation as EPA contacts: Thomas Seaton, Kevin Weiss, Michael Mitchel at (202) 475-9518. Other good sources of information are trade associations or consultants. When more specific information is available about the general permit, selection of your best option will be easier.

Do not wait too long before you start to make arrangements for either the individual or the group permit applications. The deadlines for these submittals do not allow much time to prepare the information required. Collecting storm water samples may be challenging, especially in parts of the country that typically have long, dry seasons.

Regardless of the option you select, now is a good time to assess your storm water discharges. Have you conducted tests to confirm that no nonstorm water discharges are tied into your storm water system? What are your current materials management practices? Are there some simple steps that could be taken to minimize contamination of storm water runoff by raw materials, products, or wastes?

Finally, if you discharge through a large or medium municipal storm sewer system, remember your responsibility to notify them of your discharge.

The new storm water regulations are extremely complex, and it is important that your facility develop a strategy to address them. By staying informed and taking a proactive approach, your facility will be in a better position to minimize the eventual cost of compliance.

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