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

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Cover: Huntington Environmental Systems Regenerative Thermal Oxidizer (see story on page W5). Photo courtesy of Huntington Environmental Systems Inc., Schaumburg, Illinois.



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# **Chemical Risk** Management

A Practical Approach for Implementing Risk-Based Decisions for Corrective Action

April 27 - May 1, 1998 La Fonda Hotel Santa Fe, New Mexico

A five-day course developed and presented by Risk Assessment Corporation (RAC)

formerly Radiological Assessments Corporation

# About the course . . .

This course will focus on the practical application of risk assessment techniques and risk-based decisions for corrective action being used today. A case study will be introduced on Monday and instructors will use the case study throughout the week to illustrate their topics. Emphasis will be placed on the fundamentals of risk calculations and critical data that should be collected and applied. Attendees will be provided with insight into the future of chemical risk assessment and an opportunity to learn about the state-of-the-art methodologies for estimating risk. Both proprietary and free software, including CRYSTAL BALL, MEPAS, ANALYTICA, BP Oil Company's Risk Integrated Software for Cleanups (RISC), and API's Decision Support System Software, will be available for attendees to evaluate. In addition, there will be demonstrations of the GIS software ARC/VIEW and its extensions.

# Faculty . . .

Richard L. Corsi, Ph.D., Associate Professor, Environmental and Water Resources Engineering, University of Texas at Austin. James G. Droppo, Ph.D., Manager and Senior Scientist, Multimedia Exposure Assessment Group, Northwest National Laboratory. Lesley Hay Wilson, P.E., Senior Environmental Remediation Engineer, BP Oil Company. F. Owen Hoffman, Ph.D., President, Senes Oak Ridge, Inc. Paul C. Johnson, Ph.D., P.E., Associate Professor, Department of Civil and Environmental Engineering, Arizona State University.

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For more information, call 312-988-7667 or fax 312-649-9383. Visit our course Web Page at http://www.racteam.com

# Who should attend . . .

This course will provide an overview of chemical risk assessment for individuals who are learning risk estimation methods, managers who are responsible for corrective action and risk management, those who want to expand their professional knowledge about chemical risk assessment, and individuals who are responsible for conveying risk information to the public. Some background in chemical or radiological risk assessment is recommended but not required.

Co-sponsored by A Petroleum

American Institute

# Redevelopment of Brownfield Properties: Future Property Owners/Users Proceed With Your Eyes Open

#### G. Fred Lee Ph.D, P.E., D.E.E.

G. Fred Lee & Associates, 27298 E. El Macero Drive, El Macero, CA 95618

Considerable attention is being given today to the redevelopment of hazardous chemical sites (brownfield property) as part of the federal and state Superfund program site remediation. Whitman, in an editorial in the Winter 1996 issue of Environmental Progress [6], discussed this issue from a PRP short-term perspective in which the tone of the editorial is minimizing costs and rapid remediation. While it is important to minimize unnecessary costs in site remediation relative to and needed for projected future property use, I have found as the result of being involved in a number of brownfield property remediation projects from a future property user perspective, that the shortterm, limited remediation approach that is frequently being advocated today carries with it a number of significant potential problems that should be fully understood by the PRP(s) and future property owners/users.

#### Whitman [6] states in his editorial:

"The key to the success of voluntary cleanup efforts for Brownfield sites is to tie future use of the propertv and its surrounding environs to the environmental condition and remedial approaches designed to protect against the risks of environmental hazards."

#### He further states:

"Capping urban sites through construction of an impermeable barrier at the surface provides an engineering control approach that is cost effective, environmentally sound and in concert with the future use of the Brownfieldproperty." It has been my experience that frequently PRP approaches for remediation of hazardous chemical sites are increasingly directed toward "capping" the waste management units-contaminated area.

Lee and Jones-Lee [5] have recently reviewed the potential problems of capping of waste management areas and contaminated soils as a remediation approach for brownfield properties. They point out that RCRA landfill caps:

• can be effective in preventing moisture from entering the landfill or waste management area for short periods of time, such caps as being implemented today are not necessarily effective in preventing groundwater pollution by waste derived constituents for as long as the wastes represent a threat.

•The key to the efficacy of a RCRA cap in preventing groundwater pollution is the maintenance of the low permeability layer within the cap that prevents moisture from entering the wastes and generating leachate.

•The low permeability layer of the cap is buried below a topsoil and drainage layer and therefore not subject to visual inspection for points of deterioration, holes, cracks or other areas where moisture could enter the waste through the cap.

• The introduction of a low permeability cap on a waste management unit makes monitoring of groundwaters for further pollution by the wastes unreliable. The typical groundwater monitoring approach involving vertical monitoring wells spaced hundreds or more feet apart, each with a zone of capture of about one foot can readily fail to detect the finger plumes of leachate that will be generated as a result of moisture entering the wastes through the cap.

•The post-closure care funding for capped "remediated" waste management units is only assured for 30 years. The waste will be a threat forever in many capped waste management units. There is no assurance that the funds needed to monitor, maintain and remediate groundwater pollution from the capped waste management unit will be available. This makes future brownfield property owners vulnerable to future remediation costs.

•The periodic (five year) review of the adequacy of a remediated brownfield property could readily cause brownfield property owners to have to fund additional remediation as a result of changes in the constituents of concern as well as the critical concentrations for previously identified constituents of concern.

While in-place capping of wastes in contaminated areas is one of the least expensive short-term approaches for hazardous chemical site/brownfield remediation, it carries with it potentially significant long-term issues that should and must be addressed in developing a properly remediated site. This issue has been reviewed in detail in several papers/reports (Lee and Jones-Lee, [3.4,5]) and in an ASCE conference proceedings (Dunn and Singh, [1]).

As discussed by Lee and Jones-Lee [5] it is possible, through alternative approaches, to remediate brownfield properties using caps that recognize the inherent long-term problems of todays landfill caps and prepare for their eventual failure. These approaches include the use of leak detectable low permeability layers in the cap and, most importantly, a dedicated trust fund of sufficient magnitude to monitor, operate and maintain the leak detectable cover for as long as the capped waste will be a threat. The magnitude of funding needed should include addressing all plausible worst case scenario failures including waste exhumation.

Additional information on these issues is available from papers and reports listed and made available as downloadable files from the author's Web site (http: //members.aol.com/gfredlee/gfl.htm).

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Dr. G. Fred Lee is President of G. Fred Lee & Associates, a specialty environmental consulting firm located in El Macero, California (near Sacramento). He and Dr. Jones-Lee are the two principals in this firm. Dr. Lee obtained a Bachelor's degree in Environmental Health Sciences from San Jose State College, San Jose, California in 1955. He obtained a Master's degree in Public Health, emphasizing aquatic chemistry and water quality issues in 1957 from the University of North Carolina, Chapel Hill and a Ph.D. from Harvard University in Environmental Engineering in 1960. For 30 years, Dr. Lee held university graduate-level teaching and research positions during which time he conducted over \$5 million in research on various aspect of water supply water quality, water and wastewater treatment, water pollution control and solid and hazardous waste evaluation and management. Dr. Lee has been active in contaminated site investigation and remediation for over 15 years where he has worked on sites throughout the US and in several other countries. A major thrust of his work in this area has been to evaluate the adequacy of site investigation and remediation relative to providing long-term protection of public health, groundwater resources, the environment and those within the sphere of influence of the waste management unit.

#### CONFERENCE ON BIOREMEDIATION IN MARCH 1998

A research conference, Bioremediation for Industry, co-sponsored by the Society of Industrial Microbiology (SIM) and the University of Notre Dame's Center for Environmental Science and Technology will take place on the campus of the University of Notre Dame, March 8 - 11, 1998. Practical applications of bioremediation, which uses bacteria and other microorganisms to safely break down hazardous industrial wastes, will be the focus of the conference.

Dr. Charles F. Kulpa, Director of the Center for Environmental Science and Technology, University of Notre Dame, and Terry C. Hazen of Westinghouse Savannah River Technology Center, are program co-chairs. Session topics include: regulations and risk assessments; monitoring bioremediation systems; and bioreactors and biofilters. In addition, there will be roundtable discussions on problems and developments and case studies of bioreactors/biofilters.

Researchers from academia, industry and government laboratories will address technological, regulatory and public health issues associated with biological treatment of hazardous waste sites, spills and dumps.

For more information please contact the Society for Industrial Microbiology (SIM) at Tel: (703) 691-3357; Fax: (703) 691-7991; e-mail: info@simhq.org; website: www.simhq.org.

#### REGENERATIVE THERMAL OXIDIZER CONTROLS VOC'S EFFECTIVELY

To control VOC-laden gases from two DAS (Diffused Air Stripper) basins the State of Michigan has installed a 12,000 SCFM Regenerative Thermal Oxidizer (RTO) designed and manufactured by Huntington Environmental Systems. The RTO (shown on the cover of this issue) was chosen because of its low operating cost over the lifetime of the facility. With solvent concentrations that yield very little, if any, heat value, a 95% thermally efficent RTO was judged to be the best possible choice.

The unit was installed in late 1996 at a plant in North Muskegon, MI, which had-

been used for manufacturing pharmacutical intermediates, veterinary medicines, agricultural chemicals, herbicides, dye stuffs and other products. For a significant portion of the site's operating history, waste by-products from the chemical producing processes were placed in unlined lagoons or stored in drums.

The contanimants in the air stream from the DAS basins contained VOC's, PCB's, PCE, pesticides, solvents, TCE, toulene and xylene, many of which are chlorinated compounds of low concentrations. Total VOC loading was expected to be approximately 25 lb/h.

The Regenerative Thermal Oxidizer is a three-chamber unit with manifolding and valving on one side of the vertical flow heat exchanger vessels. The purification chamber is common to all three heat recovery vessels. It operates at 1,500°F, but can be run at 1,800°F if it becomes necessary.

The system was designed with a 20 micron demister on the inlet of the system to drop out the larger liquid particles from the air stream. The regenerative thermal oxidizer was located down stream from the demister with an FRP HCL scrubber on the tail of the system. The complete system was driven by an induced draft fan located on the inlet of an atmospheric exhaust stack.

The facility has an on-site laboratory for the testing and monitoring of treated groundwater as well as atmospheric emissions from the RTO. Over the past year, it has been operating well.

For more information on the Regenerative Thermal Oxidizer please contact Huntington Environmental Systems, Schaumburg, IL.

#### EPA APPOINTS AICHE MEMBER TO TRI COMMITTEE

The Environmental Protection Agency (EPA), on the recommendation of AIChE's Government Relations Committee, has appointed AIChE member Krisztina Bordacs to serve on its committee reviewing the reporting requirements of the Toxics Release Inventory (TRI). She started her two-year term in October 1997. EPA's 24-member Toxics Data Reporting Comittee was chartered to improve the information available to communities about emissions of toxic substances from industrial facilities and to streamline the reporting requirements for businesses.

Brodacs, a senior environmental engineer with Smith Kline Beecham in King of Prussia, Pennsylvania, is responsible for the environmental technology needs of the company's facilities. She is also a member of the TRI task force of AIChE's Government Relations Committee.

#### FIRST SEA WATER POWER STATION UNDER CONSTRUCTION IN JAPAN

The Ministry of Foreign Affairs of Japan recently announced that the world's first experimental power station that uses sea water is being built north of the island of Okinawa. This is an unprecedented attempt to find out whether it is feasible to use sea water in a power station using the pumpedwater principle. Should the trial plant be successful, Japan, with its long coastline may solve its ongoing problem of finding suitable sites for power generation.

Japan is searching for alternative methods for power generation because its 53 power plants and plutonium waste cycle have been coming under increasing criticism due to accidents and dangers of waste handling and transport. If the experiment proves successful areas near Tokyo, such as Izu, could become sites for power generation.

The plant will operate by raising the brine during the night, when electricity-consumption rates are low, and release it from a storage reservoir on high land to generate power during the day. Water will be lifted by a pump to a reservoir 150 m above sea level and released en masse to generate electricity at an underground facility before being returned to sea. Power can be supplied when needed at any time after the preliminary pumping work is complete. Maximum capacity is 30,000 kw for six hours, enough to supply households containing 30,000 persons.

Nonetheless, many technical hurdles remain. Turbines and other generation equipment need to be protected against sea water corrosion. The surrounding environment must also be protected against saline damage.

Designers have proposed using strong fiberglass-reinforced plastic for the conduits

that direct water to the turbines and constructing the actual turbines from special stainless steel. The plant is scheduled to be operational by the spring of 1999.

#### EPA PROPOSES RULE TO ELIMINATE POLLUTANTS FROM PULP AND PAPER MILLS

The Environmental Protection Agency (EPA) is proposing two amendments to 40CFR Part 430, the Pulp, Paper and Paperboard Point Source Category. The proposed rule will virtually eliminate dioxin discharges into waterways and reduce many other toxic pollutants into air and water from pulp and paper mills that produce bleached paper products. According to EPA administrator Carol M. Browner "This action puts us well on our way to cleaning up more than 70 rivers and streams throughout the nation."

The first amendment affects only existing direct discharging mills in Subpart B (Bleached Papergrade Kraft and Soda subcategory) that chose to enroll in the Voluntary Advanced Technology Incentives Program being promulgated in the final Pulp and Paper "Cluster Rules."

The second amendment would authorize mills in Subpart B to demonstrate compliance with applicable cloroform limitations and standards (also being promulgated in the "Cluster Rules) in lieu of monitoring at a fiber line, by certifying that the fiber line is not using elemental chlorine or hypochlorite as bleaching agents and that they also maintain certain operational conditions specified in the proposed regulation. The EPA says that this second amendment would reduce the reporting burden for those mills that choose to certify.

Mills volunteering for the program will be subject to more stringent reductions, but, in return, will receive rewards for their participation, such as additional compliance time. The rule is a coordinated, simultaneous effort under the Clean Air Act and the Clean Water Act that allows mills to select the best combination of pollution prevention and control technologies to achieve pollution reductions.

Commentson the proposal, as well as information and data regarding TCF processes, should be sent in triplicate to Mr. J. Troy Swackhammar, Office of Water, Engineering and Analysis Division (4303) U.S. Environmental protection Agency, 401 M Street, S.W., Washington D.C. 20460; e-mail: swackhammer.j-troy@epmail.epa.gov.

#### AICHE OFFERS COURSE ON DESIGNING AIR POLLUTION CONTROL EQUIPMENT

The American Institute of Chemical Engineers (AIChE) is offering a course on Designing Air Pollution Control Equipment to take place in New Orleans, March 6-7, 1998. The course can benefit not only air pollution control specialists, design engineers needing an introduction to pollution control methodology and maintenance engineers responsible for air pollution control equipment or monitoring devices; supervisors responsible for monitoring compliance; consultants looking for a review of current problems and trends.

Attendees can gain a broad view of the subject and the principal mechanisms involved in the removal of gaseous and particulate matter from stationary sources. In addition they will focus on sizing equipment and the best method for eliminating toxic substances. Participants will familiarize themselves with the latest monitoring devices, discuss relevant problems and uncover technological solutions.

The fee is \$845 for AIChE members and \$945 for non-members. For more information, or to register, please contact the AIChExpress Service Center at 1-800-242-4363; fax: (212) 705-8400; e-mail: xpress@aiche.org.

# KNOTWEED PLANT HELPS CLEAN BRINE FROM CONTAMINATED SITES

A study conducted by Ohio Unviersity has revealed that knotweed can help clean oil drilling sites contaminated by brine spills according to an ENN Newswire report. Brine, water saturated with up to 10 times the salt contained in seawater, is toxic to plants. The plant, a form of Buckwheat, Polygonum aviculare L, actually helps remove the salt. Soil tests showed that the weed actually reduced the saline .

Irwin Ungar, Professor of Environmental plant Biology at Ohio University and co-author of the study said "At the site we studied, the brine spill occurred in 1989 when workers were pumping the salt water out for storage... Currently, soilcontaminated by brine must be removed and landfilled. " Scientisits a year later found all the vegetation dead but knotweed growing in and around the pheriphery of the spill. Four years later, when the salt content was still about 2% above normal, knotweed was thriving inside the spill area.

Soil tests showed that the weed reduced the saline content and that the site will eventually return to its pre-spill state thanks to the knotweed and dilution achieved through rainfall. "Using this or some other saline-tolerant plant to remove salt from the soil through natural means would be more environmentally and economically desirable," continued Professor Ungar.

The species of knotweed studies is closely related to a much more aggressive variety found in Japan. It is a ground-covering leafy plant bearing small pink flowers. It is not as salt-tolerant as plants found in salt marshes or coastal areas but its wide habitat range makes it an ideal candidate for soil conservation efforts.

#### MTU AND DIPPR COLLABORATION PROVES SUCCESSFUL

In partnership with AIChE's Design Institute for Physical Property Data (DIPPR), Michigan Technological University's Chemical Engineering Department has developed a major focal point in areas of environmental thermodynamics, physical property data, and data estimation methods. The critically reviewed experimental data values and physical property estimation techniques are of

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particular interest to chemical process industry design engineers in the environmental, process safety and health arenas.

Over the past five years Michigan Technological University has been the prime contractor for two major DIPPR projects. Project 911 entitled the Environmental, Safety and Health Data has compiled and carefully evaluated data for over 600 chemicals of regulatory interest from both environmental and safety perspectives. Fifty five properties have been investigated including oxygen demand perameters, and toxicity. Project 912 has evaluated existing techniques for estimating the properties of interest in Project 911. Based upon comprehensive studies, predictive methods have been recommended for each peoperty, with an emphasis on molecular structure based techniques.

The Property Estimation and Retrivel System (PEARLS) implements these methods in software form with an easy-to-use graphical interface. These two properties have served as the centerpiece of the thermodynamics and physical properties effort at MTU, which include projects for the Environmental Protection Agency (EPA), the National Instute of Standards and Technology (NIST) and the National Aeronautics and Space Administration (NASA).

#### DENVER TO RECLAIM TOXIC GROUNDWATER FROM SUPERFUND SITE

The Environmental Protection Agency (EPA) recently approved a proposal by the City and County of Denver, Waste Management Inc., and Chemical Waste Management of Colorado for the Metro Wastewater Reclamation District to treat approximately 14,400 gal/d of pretreated groundwater from the Lowry Superfund Site.

The groundwater will contain some leachate materials and will be pretreated at the site before being discharged to a yet-to-be -built sewer for eventual final treatment before the Metro District's treatment plant north of Denver. The pretreated Lowry Site groundwater represents less than one-ten thousandth of the 150 million gal/d of wastewater the Metro District treats -97% of which is domestic wastewater.

The Metro District will regulate the Lowry Site groundwater under the federal Clean Water Act's industrial waste pretreatment program. The treated effluent must meet stringent industrial waste discharge standards as well as federal and state drinking water supply standards before it is discharged into the South Platte River.

#### ENVIRONMENTAL CONFERENCE SLATED FOR DUBROVNIK NEXT MAY

The International Union of Pure Applied Chemistry (IUPAC) is sponsoring an International Conference on "Degradation Processes in the Environment" to take place May 24-28, 1998 in Dubrovnik, Croatia.

The primary goal of the conference is to present and evaluate the state-of-the-art in environmental degradation technologies. Attention will be paid to the following areas: kinetics and reaction mechanisms, assessment of availability and quality of degredation data, and qualitative/quantative modeling of degradation processes. The conference will provide a scientific basis for recommendation on data quality standards, estimation of degradation rates, and identify the major gaps in knowledge where future research is needed.

A second goal is to enable and stimulate interactions and communication between research institutions, government agencies and industry. The conference will provide a forum for exchange of information and discussion of environmental problems with emphasis on application of research results in improving risk assessment procedures, environmental protection, and pollution prevention. A round-table discussion is planned on assessment of degradation rates with respect to data quality, estimation methods, and applicability.

The conference topics are: atmospheric degradation processes; degredation processes in water and soil; degradation data - sources and quality; modelling degradation processes, and application of research results in environmental management.

For more information please contact Dr. Aleksandar Sabljic, Rudjer Boskovic Institute, P.O. Box 1016, HR-10001, Zagreb, Croatia. Telephone: +385-1-456-1089; Fax: +385-1-468-0084 or +385-1-468-0245; e-mail: sabljic@rudjer.irb.hr.

# EPA CLARIFIES CERTAIN PROVISIONS OF THE CLEAN AIR ACT

The Environmental Protection Agency (EPA) recently stated their interpretation of the accident prevention provisions of its regulations issued under Section 112 (r) of the Clean Air Act. The information published in 62 *Fed. Reg.* 45134 (August 25, 1997) also clarified that certain reports do not have to be reported under section 8(e) of the Toxic Substance Control Act or its implementing rules.

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Chemical engineering from A to Z

#### ACTIVATED SLUDGE TREATMENT OF INDUSTRIAL WASTEWATER

W. Wesley Eckenfelder and Jack L. Musterman, Technomic Publishing Company, Lancaster, PA, (1995), 281 pages, [ISBN No.: 1-56676-302-9], U.S. List Price: \$85.00

As the authors acknowledge in their Preface, there are a number of superb books already available on the general topic of biological wastewater treatment. Nonetheless, this new offering by Wes Eckenfelder and Jack Musterman provides a thorough and well-prepared summary of the current state-of-the-art for industrial wastewater treatment using activated sludge systems. In many respects, the look and feel of this new text is comparable to one of Wes Eckenfelder's prior classics, with a balanced mix of theory and pragmatic insights drawn from many decades of hands-on familiarity. However, the included topics not only cover the usual basics, but also a variety of current and upcoming issues. After reviewing the fundamentals of waste characterization, pretreatment, and general activated sludge processing, these authors have then included timely sections on bioinhibition, VOC stripping, oxygen transfer, and a variety of advanced treatment schemes. The topic of abnormal temperatures is also addressed, particularly in the context of hightemperature wastes and reactor environments and their impact on biochemical performance and behavior. The experience and depth of understanding enjoyed by these authors is readily evident throughout the book. Simply put, this is a book well worth adding to one's collection.

James E. Alleman, Ph.D Professor of Environmental Engineering School of Civil Engineering Purdue University West Lafayette, IN 47907

#### COLUMN FLOTATION PROCESSES, DESIGNS, AND PRACTICES

Julius B. Rubinstein, Gordon and Breach Science Publishers, Basel, Switzerland, (1995), 296 pages, [ISBN No.: 22-88124-917-5], U.S. List Price: \$95.00.

Rubinstein's book addresses the beneficiation of economic minerals (ores and coal) by surface chemical separation techniques as implemented in flotation columns. The principal environmental impact of this technology is almost certainly the upgrading of coal by removal of ash and sulfidic sulfur. Rubinstein chooses numerous examples from coal technology throughout the book. His position at the Institute of Solid Fuels Preparation in Moscow puts him in an excellent position to discuss the beneficiation of coal and to provide the reader with insight into the extensive Russian literature on column flotation techniques.

After a brief historical introduction to flotation and a short discussion of column flotation in Chapter 1, the book turns in Chapter 2 to the discussion of the various types of flotation columns and their major components. Rubinstein provides numerous descriptions and many excellent drawings of equipment. References are somewhat sparse, perhaps because much of this information is not in the open literature. Chapter 3 gives a detailed description of bubble formation in flotation columns, discussions of various types of aerators, and quite a bit of information on coal flotation.

Chapters 4 and 5 address experimental and theoretical aspects of column aerodynamics. Tracer experiments and their mathematical analysis are discussed in depth. Other topics include gas holdup and particle motion in flotation columns, and mixing in two-phase systems. This material is presented with a fairly high degree of mathematical rigor. Chapter 6 deals with experimental investigation of the process of flotation in columns. Rubinstein describes in detail a pilot test set-up he has used. The effects of operating parameters on performance are discussed, and the chapter includes lots of experimental results and descriptions, including a number of full-scale field installations.

The kinetics of column flotation and aspects of column modeling are presented in Chapter 7. Rubinstein gives a rather detailed discussion of the modular development of flotation column models which is one of the highpoints of the book. Chapter 8 continues in a mathematical vein as it presents methods for scaling up flotation columns.

A rather abbreviated treatment of structure and mass transfer in flotation froths is given in Chapter 9. A discussion of the surface chemical aspects of flotation in this chapter would have been interesting; the book does not address the surface chemistry of these flotation separations.

Chapter 10, on column flotation practice, discusses numerous commercial applications of the technology throughout the world. Rubinstein's inclusion of a good deal of Russian applications provides a valuable window onto the work in this area which has been performed in the former Soviet Union. Chapter 11, the last chapter, provides a very brief and qualitative discussion of column flotation control - sensors and control algorithms. Perhaps this treatment will be expanded in a later edition of the book.

This book is a "must have" reference for anyone involved in ore or coal processing. The mathematical sections, while difficult, reward attention and effort. The numerous descriptions of apparatus and the accompanying drawings are extremely informative, as are the discussions of flotation column installations throughout the world.

David J. Wilson, Ph.D Senior Research Fellow Eckelfelder Inc. 227 French Landing Drive Nashville, TN 37228

#### ENVIRONMENTAL AND HEALTH & SAFETY MANAGEMENT: A GUIDE TO COMPLIANCE

Nicholas P. Cheremisinoff and Madelyn L. Graffia, Noyes Data Corporation, Park Ridge, NJ, (1995), 502 pages, [ISBN No.: 0-8155-1390-9], U.S. List Price: \$78.00

Environmental and Health and Safety (EH&S) Managers are faced with the responsibility of handling both environmental policy/issues and the safety of workers within their organizations. Over the past two decades, the growth of safety departments, and the increase in the number of environmental compliance specialists and other technical staff associated with waste management and the associated environmental issues have been phenomenal. However, the last several years has seen the downsizing of corporate America, and consequently, an increased segment of these activities has been the responsibility of middle and lower level management. Organizations are moving toward a single management entity, the EH&S manager, whose responsibilities require an extensive knowledge of both environmental statutes and OSHA standards.

The primary intent of this book is to provide a concise yet comprehensive source on compliance issues for the EH&CS manager. It provides a single useful reference on both the environmental regulations and the safety standards with which the industry is expected to comply. In addition, the book provides valuable information on the management practices for on-site hazardous materials handling and identifies the requirements for hazard communication and related training programs for employee safety.

The first two chapters provide information on the related EH&CS regulations and identify the need for management of compliance in both the environmental and occupational safety areas. Focus is primarily on hazardous materials and the various regulations concerning occupational and environmental safety associated with their manufacture, use, transportation, waste handling, and cleanup of unintentional disposal. The related federal regulations are clearly identified and their key provisions summarized. The second chapter focuses on the management of facilities and the laws associated with the operation of hazardous waste sites including regularly scheduled assessments, cleanup, and transfers of responsibility. The chapter outlines the requirements of various Federal and State regulations focused on the maintenance of air and water quality. The chapter also includes a useful section on the importance of regular audits, related costs, the process of engaging consultants, and the liabilities associated with consultants and insurance organizations.

Chapters 3 and 4 relate to the safe handling, storage, and disposal of hazardous chemicals. Chapter 3 provides a concise summary of the chemistry of hazardous materials and describes the need for a fundamental understanding of their physical, chemical, and biological properties. The properties related to the four segments of the National Fire Protection Administration are discussed, and a segment on the determination of the compatibility of chemicals is a valuable additional piece of information for the busy EH&S manager. Chapter 4 stresses the safety management practices related to the storage, use, transport, and disposal of hazardous materials, including radioactive species. The use of Materials Safety Data Sheets, proper labeling of chemicals to identify their hazards, the need to select appropriate personal protective equipment (PPE), and the proper waste handling procedures and emergency management responses are emphasized.

Chapter 5 addresses the Resource Conservation and Recovery Act and describes the EPA classification of hazardous wastes. Information on hazardous waste generators, waste accumulation, regulations pertaining to laboratories, waste determination, and waste analysis planning is also provided.

Chapters 6 to 9 are on topics introduced in chapters 3 and 4. Chapter 6 dwells on hazard communication and provides a summary of the "right-to-know" law. Listing of hazardous chemicals, proper labeling, and the training of workers in accordance with the right-to-know requirements are stressed. Readers of this chapter will also gain understanding of the information in hazardous substance fact sheets, the OSHA 200 log of injuries and illnesses, and the common methods used to recognize, evaluate, and control employee exposure to hazardous materials. The evaluation of the seriousness of a given hazard, the toxicology of hazardous materials, the measurement of exposure, and analytical techniques for the determination of hazard concentrations are discussed. Prevention through substitution, engineering controls such as ventilation, and other administrative measures are also considered. The chapter also includes a section on the hazards of radioactive materials.

Chapter 7 relates to process safety and hazard

analysis, the process of hazard analysis, and various evaluation techniques such as failure modes and effects analysis, fault tree analysis, and event tree analysis. Chapter 8 discusses the requirements for hazardous waste transportation, and chapter 9 relates to the treatment, disposal and waste minimization and storage practices.

Chapter 10 focuses on the management of underground storage tanks and includes measures to prevent and detect releases, the general operating requirements, responses to leaks or spills, and closure and post closure requirements. Chapter 11 discusses the requirements of the Federal Insecticide, Fungicide and Rodenticide Act.

Managing worker PPE is the focus of the final chapter of the book. It discusses the development of a PPE program, the selection of proper respiratory equipment and clothing, and the related training of employees for their proper use and maintenance. A valuable section of this chapter discusses heat stress. The book concludes with a glossary of EH&CS terms and abbreviations commonly used by EH&CS managers.

In summary, this book would be a valuable reference source for EH&S managers. The authors are concise and yet provide a broad background and considerable technical detail, including the relevant regulations for any EH&S manager to quickly focus on the critical issues associated with the task associated with the storage, use, or disposal of hazardous materials. I strongly recommend that EH&S managers seriously consider adding a copy of this book to their reference library.

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

# COMBUSTION TECHNOLOGIES FOR A CLEAN ENVIRONMENT

Maria da Graca Carvalho, Woodrow A Fiveland, F.C. Lockwood, and Christos Papadopoulos, Gordon and Breach Publishers, Amsterdam, The Netherlands, (1995), 838 pages, [ISBN No.: 2-88124-619-2], U.S. List Price: \$125.00

There is a basic conflict between the use of energy to support the world's economies and standard of living and the environmental protection of air quality to sustain the world's life. The conflict must be placed in perspective to better analyze and understand the challenge of this situation.

The goal of this handbook is to describe, compare, and evaluate new combustion technologies, which maximize energy conversion, while minimizing undesirable emissions. The handbook contains selected papers from the First International Conference on Combustion Technologies for a Clean Environment, held in Vilamoura, Algarve, Portugal, on September 3-6, 1991. The papers represent 21 countries, mainly from Europe, North America and Asia.

The 54 papers contained in this handbook have been grouped into ten parts, based upon subject matter:

- Strategies: Now and in the Future
- Pulverized Coal Combustion
- Oil Combustion
- Gas Combustion
- Gas Fired Systems
- Biomass Combustion
- Fluidized Bed Combustion
- Incineration
- Internal Combustion Engines
- Reaction Kinetics

The papers in the handbook are generally well-written and peer-reviewed. They cover many different aspects of the field and have been well integrated to provide a worthwhile addition to the literature.

This handbook is recommended for managers, engineers, and scientists in the energy field to broaden their perspective in understanding the relationship of technology in solving this complex problem. Personnel in industry, government, and academia will benefit from this international collection of papers in the energy field.

Charles A. Wentz, Jr. Ph.D., P.E., CSP President International Scientific Management Inc. 5953 Old Poag Road Edwardsville, IL 62025

#### HAZARDOUS AIR POLLUTANTS: ASSESSMENT, LIABILITIES, AND REGULATORY COMPLIANCE

Jeffrey W. Bradstreet, Noyes Data Corporation, Park Ridge, NJ, (1995), 385 pages, [ISBN No.: 0-8155-1386-0], U.S. List Price: \$64.00

Over the past several years, hazardous air pollutants (HAP) have become a major area of concern for industry. The regulatory requirements and the potential liabilities associated with the emission of HAP add a significant burden to industries already loaded down with the costs of environmental compliance. After the 1984 incident in Bhopal, India, several states in the U.S. introduced legislation to govern the emission of hazardous pollutants, and in 1990 Congress passed significant amendments to the Clean Air Act. Industrial facilities are constrained by these regulations to evaluate, control, monitor, and assess risk for a variety of listed chemicals considered HAP. Title III of the Clean Air Amendments Act and several state regulations address over 600 HAP Compliance deadlines are being developed and are scheduled to be completed by 2003.

This book provides valuable insight into the regulatory requirements affecting sources of HAP. It discusses available methods for the inventory and measurement of emissions, and reviews methods for the determination of potential risks and liabilities due to the emission of HAP. It also discusses available options for emission reduction and provides a means to establish a viable compliance program. The book is well illustrated and has several useful tables and appendices, as well as references for those who are interested in exploring this area further.

Chapter 1 consists of a general introduction and briefly discusses the origin of the early legislation on air pollution, tracing its progress through the Clean Air Act of 1963 up to the present. Lack of real progress in emissions control resulted in the 1970 Clean Air Act Amendments, which established National Ambient Air Quality Standards (NAAQS) for criteria pollutants and regulations for a new category of HAP which included asbestos, beryllium, and mercury. Over the years other Amendments which affected the regulation of criteria pollutants came into place in 1977. Following the incident at Bhopal and legislation by individual states the 1990 Amendments to the Clean Air Act were enacted. Title III of these Amendments included 189 HAP, and required the EPA to promulgate technology based emission standards based on the best available control technology. Chapter 2 provides the regulatory definitions of hazardous air pollutants and summarizes the physiological effects and classification of pollutants based on their potential to cause hazardous effects. In any case, the full spectrum of regulations controlling a potentially hazardous material needs to be addressed; and to avoid litigation and potential liability issues, the material safety data sheet should identify the hazardous components in the material and include any toxic or carcinogenic properties identified in animal studies.

Chapter 3 describes the extensive requirements of Title III to the Clean Air Amendments Act of 1990, defines the differences between major sources and area sources, and evaluates emission reduction technologies and the risk management plans associated with these emissions. The EPA has yet to come up with residual risk emission standards, providing "an ample margin of safety," or with an enforceable means of reliable continuous monitoring of stack emissions for HAP. The author indicates that industry will be hard pressed to monitor and evaluate the risks associated with several HAP, and to achieve compliance with the maze of confusing requirements.

Chapters 4 and 5 describe other Federal regulatory requirements and those promulgated by individual states. Industrial organizations will have to sort out the overlapping areas and develop their own approach to compliance. Chapter 6 lists sources of hazardous air pollutants at industrial facilities by various source categories.

Chapter 7 focuses on the inventory of HAP and describes several approaches which may be applicable. It stresses the need to evaluate reporting requirements based in the total emission inventory and refers to guidance documents from the EPA. The author stresses the pollutant release limits at which various reporting may be required but suggests that upper management should always be aware of total plant emissions so that they may plan appropriately for future compliance as the nature or quantities of emissions change.

Chapter 8 indicates the increased need for the measurement of hazardous air pollutants caused by the Amendments of the Clean Air Act and the associated regulations imposed by the states. These measurements are necessary to determine the emissions, ambient air quality, and associated health risks. The limited data on ambient air quality and emissions data on hazardous air pollutants make a ranking of pollutants difficult. The chapter evaluates the different approaches available and make an assessment of their relative merits. Documents describing procedures acceptable to EPA for the dispersion modeling of the hazardous air pollutants and siting of monitors are cited in the reference.

Chapter 9 describes the assessment of health risks. This involves a combination of good judgement and extrapolation of the limited data that are available to forecast human exposures and the long-term effects of such exposures. the EPA-approved air dispersion models and risk assessment models are described to evaluate the exposures and to determine risks, allowing corrections for variability of exposure rates and times. The need for a clear definition of assumptions is stressed, and the author indicates that the many factors which determine exposure-related risks may result in widely varying results based on the nature of the assumptions. As corrective measures, some of which could be expensive, are necessary to curtail exposures, it is expedient that assessments be made with due care to identify the risks as close as possible to reality. Chapter 10 discusses the nuisance characteristics of HAP primarily focussing on odor. Methods to measure the concentrations of these air pollutants and to dispose of them are also indicated. Chapter 11 provides a brief review of the liabilities associated with HAP, both from the standpoint of regulatory requirements and other areas of potential litigation.

Chapter 12 focuses on emission reduction alternatives and includes approaches to pollution prevention or add-on control technology. The Amendments to the Clean Air Act of 1990 provide several alternatives to eliminate or reduce the source of emissions. Techniques vary and are dependent to a large extent on the nature of the operations and the types of materials which are released to the environment. The most significant of the proposed requirements is the implementation to the "maximum achievable" control technology standards for industry manufacturing synthetic organic chemicals. The use of both add-on and pollution prevention techniques is permitted to achieve compliance with the standard. It is clear that any designs to control HAP must include a thorough inventory of all the pollutants and an assessment of the most viable technology options to achieve compliance with the standards.

The last chapter of the book identifies the requirements for the establishment and maintenance of an effective program for HAP management. These include a thorough inventory of emissions, an assessment of compliance with the current requirements, review of state permitting schedules and facility operating plans, a review of finalized regulations, and completion of health risk assessments. Options for reducing emissions and tracking, monitoring, and reporting them are listed.

In summary, this book would be a valuable reference source for those involved in developing plans for the establishment and maintenance of a management strategy for HAP. The author has made a sincere effort to turn a rather tedious task into a less onerous one. The impact of the various regulations and the information required to achieve compliance are clearly identified.

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

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# A Guide to Indoor Air Quality Sites on the World Wide Web

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#### Ashok Kumar

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#### INTRODUCTION

All of us face a variety of risks to our health as we go about our day to day lives. Poor indoor air quality or environment has been shown to result in headaches, respiratory infections, wheezing, nausea, dizziness, respiratory allergies, influenza, colds, measles, pulmonary tract infections, Legionnaire's disease, and other ailments. Driving in cars, flying in planes, engaging in recreational activities and being exposed to environmental pollutants all pose-varying degrees of risk. Some risks are simply unavoidable. Some we choose to accept because to do otherwise would restrict our ability to lead our lives the way we want. Indoor air environment is one risk that you can do something about.

There are many steps one can take to improve and control your indoor air environment. The steps will depend on the environmental conditions that currently exist in your home or office or plant. If you knew why indoor air environment was unhealthy and what you could do to make it healthy again, then you could control the indoor air quality and, subsequently, the symptoms.

A significant number of companies have realized the importance of maintaining good indoor air environment in their buildings. Most companies investigate indoor air quality complaints as they arise and a few monitor indoor air environmental indicators regularly. However, the current trend for organizations is the establishment of an indoor air environmental management plan for their facilities which integrates monitoring, operations and maintenance, building staff training, and building renovation activities.

The growth of information available on the Internet and the World Wide Web (WWW) is explosive. New users around the world are signing on by the thousands. Therefore, it is more important than ever for environmental professionals to keep tabs on those sites that can offer much-needed information at any hour of the day or night.

Several papers have been published in this journal on the sites available on various topics in environmental field (1, 2, and 3). The

purpose of this paper is to provide a guide of useful indoor air quality sites on the WWW.

More than 1000 Web sites related to indoor air environment quality were reviewed for this paper. A list of 44 sites was prepared to help you find useful information in this field. The paper is divided into two sections: (1) Services and Products, (2) Training/Courses, Technical Organizations, Government Sites and Publications. Some of the sites provide general information on indoor air environment and its impact on individuals and the others have more specific information, such as how to take corrective action. As with any information source, knowing what you are looking for - and the general area where to find it will increase your chances for productivity and success.

As Internet is in transition from being a mere curiosity to a technology asset, the newcomers to the Web and the Internet should be aware that the information they find -like other information - is only as good as its sources. Just because something appears on the World Wide Web, it is not necessarily true or authentic. As with so many other things, it is "buyer beware".

#### SITES FOR SERVICES AND PRODUCTS

Web Site: www.hygeia-env-inc.com/ e-mail: info@hygeia-env-inc.com

Hygeia Environmental Inc. (HEI) is multi-disciplined environmental laboratory and indoor air quality specialist. They offer a wide range of environmental laboratory services and IAQ site investigations for hospitals, colleges, public schools, commercial buildings, and homeowners. They also supply a variety of clients with environmental equipment rental.

#### Web Site: www.ebdinc.com/

Anabec Inc. based in Clarence, NY maintains the site. The Anabec provides services such as lab testing, remediation of contaminated building surfaces, and so on. Based on laboratory recommendations, a trained representative can spray your building surfaces (acoustical ceiling tiles, painted brick, and carpeting) to remediate contaminated problems. The web site provides necessary information on indoor air quality related symptoms, causes and possible solutions using their system.

#### Web Site: www.teamkd.com/

K.D. Engineering Co. provides specialized services in the field of indoor air quality related to testing, adjusting and balancing. The company designed/introduced IAQ instruments (KD 300 Series, KD 400 Series) in last three years, to assist practitioners in the IAQ field. The Web site provides detailed information about the instrumentation such as technical details, how to use it and how to get it.

#### Web Site: www.cascadewater.com/

Cascade Water Services provides services including water treatment and cleaning (cooling towers, boilers, chillers, piping, closed systems, water/air condensers, air handlers and ducts), chemical sales and installations, consulting and laboratory services, rebuilding and repair, and indoor air quality (IAQ testing, duct cleaning and encapsulation).

#### Web Site: www.comlynx.xom/iaqindex/iaqintrv.htm

Indoor Air Services, Inc maintains this site. The company has developed variety of educational packages (video plus manuals) on how to improve indoor air quality for HVAC contractors, Industrial Hygienists, Duct Cleaners, and School Districts, etc. The information on the variety of programs can be viewed on this site.

#### Web Site: www.titus-hvac.com/

TITUS is one of the largest manufacturers of HVAC products. They design and manufacture air distribution products for HVAC systems. These products can provide higher comfort levels and improve indoor air environment in almost any building. The software program related to various company activities and design/application can be downloaded from this Web site.

#### Web Site: www.shelter-mn.com/

Shelter companies (Shelter Source and Shelter Supply) designs and manufacture ventilation equipment and specialized energy efficient building products. The Web site provides an easy to follow how-to guide for all aspects of building science and technology. The product catalogue is also available on this site.

#### Web Site: unionac.com/

A.C. Union Air Conditioning, Inc. is a multi-faced HVAC designbuild mechanical contractor. They provide customized HVAC systems (planning, designing, and installation) for commercial and industrial facilities worldwide. Information related to type of ventilation systems and their advantages, design features related to indoor air environment and more can be viewed on this Web site.

#### Web Site: www.metrosonics.com/airqmon.html

The Web site describes a complete product line related to indoor air quality monitoring instrumentation offered by Metrosonics Inc. These monitors can be viewed on the site and is ideal for numerous applications, such as investigating sick building syndrome and indoor air quality complaints, analyzing HVAC operation, and verifying compliance with standards and regulations. In addition, Metro sonic's offers IAQ related software which has many powerful features such as data retrieval and storage, database searching and automatic calculation of air exchange rate.

#### Web Site: members.aol.com/IAQatOMS/index.html

The Web site describes the capabilities of OMS Laboratories, Inc. They use state-of-the-art instrumentation for analyzing indoor air environment samples. Gas chromatography and mass spectrometry are used for specific molds and mites contamination.

#### Web Site: www.chelsea-grp.com/

Chelsea Group Limited (CGL) is an environmental consulting information services and technology company with a specialty in indoor air quality. The site provides links to US government, private and international sites in the field of indoor air environment. Their newsletter "INVIRONMENT" published monthly can be viewed on the site. It provides latest regulatory and standard setting news and articles written by prominent leaders in the industry on indoor air environment. Reference documents on how to improve indoor air quality in hotel/motels, restaurants/lounges, etc. and information on a self-paced video, which provides detailed direction for IAQ professionals on how to conduct an investigation into the building environment can be viewed on this site.

#### Web Site: www.airdoctors.com/

If you are seeking information concerning the adverse health effects of poor indoor air environment, then this is one of the best Web sites to view. Air Doctors, Inc maintains the site. They have the cure for sick building syndrome (SB S), tight building syndrome (TB S), building related illnesses (BRI) and generally poor indoor air quality.

#### Web Site: americanclean.com/index.html

American Services Corporation (AS C) offers a wide range of engineering consulting and management services directly related to indoor air quality. The company also provides ductwork and HVAC system cleaning services. Detailed information about company activities and on indoor air environment issues can be viewed on this site.

#### SITES FOR TRAINING/COURSES, TECHNICAL ORGANIZATIONS, GOVERNMENT SITES AND PUBLICATIONS

Web Sites: www.environ.com/iaq\_trn2.htm www.environ.com/epa\_iaq2.htm www.environ.com/iaqempr.htm www.environ.com/iaqempr.htm

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These sites are maintained by Environment Support Solutions. They offer a complete line of products and services for environment management issues, including training, consulting, site compliance surveys and software for HVAC contractors and facility managers.

Environmental Support Solutions also maintains HVAC Mall on the web site. It is resource for people looking for heating, ventilating, air conditioning and refrigeration products and services. One can find information from manufacturers, distributors, representatives, contractors, consultants, educational institutions, associations, publications and software developers who offer HVAC/R and other related products and information.

#### Web Site: www.envirovillage.com/Training/MEHRC

Mid-Atlantic Environmental Hygiene Resource Center (MEHRC) offers a wide range of courses on various IAQ topics. The web site contains course description and current schedule.

#### Web Site: www.aivc.org

Air Infiltration and Ventilation Center (AIVC) maintains this site and viewers can learn about AIVC publications, including recent report on energy-efficient ventilation. This site provides an access to the center's data on ventilation issues, including information services, technical analysis and database of articles on indoor air/environment quality.

#### Web Site: www.cyberus.ca/~dsw/

International Society of Indoor Air Quality and Climate (ISIAQ) maintains a Web site and is dedicated solely to issues of the indoor environment. The site contains recent news related to IAQ, notices of upcoming meetings and lists research/task force activities.

#### Web Site: www.ACGIH.org/

American Conference of Governmental Industrial Hygienists (ACGIH) provides latest information on training courses, upcoming conferences and seminars and other special events in the field of indoor air environment. The Web site is a very helpful resource for environmental specialists (ventilation systems, health and safety, indoor air quality, and more...). Condensed versions of ACGIH publications are available on the site.

#### Web Site: greenbuilding.ca/

The Green Building Information Council (GBIC) brings this web site to you, a Canadian non-profit organization whose mission is to disseminate information about energy and environmental issues in the building sector. GBIC itself is a small organization with extensive international links and through this site one can view a broad range of information from other sources and organizations around the world, all of which are separately identified.

#### Web Site: www.ashrae.org

American Society of Heating, Refrigerating and Air-conditioning Engineers (ASHRAE) maintains a Web site that allows users to view current activities, including standards activities and upcoming meetings/forums. Their Web site also gives link to the on-line edition of the ASHRAE journal. ASHRAE plans to continue to use the site to post proposed standards for users to download, as it did recently with the proposed revision to Standard 62 related to indoor air quality and Standard 90.1 related to building energy efficiency. Once the public comment period closed, these standards were removed from the site. The ASHRAE bookstore catalogue allows you to order on-line codes, standards, guidelines, and handbooks.

#### Web Sites: www.osha.gov

www.osha.gov/govsites.html

The Occupational Safety and Health Administration (OSHA) web site offers publications, information on current and future programs, statistical data, as well as compliance assistance. The Web site gives link to other government sites/agencies.

#### Web Sites: www.cdc.gov/NIOSH/homepage.html

www.cdc.gov

www.cdc.gov/epo/mmwr\_wk.html www.cdc.gov/cgi-bin/mmwrsearch.pl

These Web sites can provide a wealth of information from National Instirute of Occupational Safety and Health (NIOSH) and Centers for Disease Control (CDC) on health hazard evaluation programs, current disease topics (Legionnaires' disease, Legionella, tuberculosis or carbon monoxide poisoning) related to indoor air environment. Users can download such things as NIOSH's questionnaire for indoor air investigations. The back issues of Morbidity and Mortality Weekly Reports (MMWR) can be searched and viewed on one of these sites. These are important sites, if one would like to keep updated on NIOSH and CDC research activities. Eventually, the outcome from these research activities forms the basis for US government regulations.

#### Web Site: www.iaqpubs.com/

Indoor air quality related publications could be viewed on this site. The web site is kept updated and provides current valuable news and information on topics related to indoor pollution, healthy buildings, occupational health and safety and lead poisoning prevention.

Web Sites: www.epa.gov/iaq/

www.epa.gov/iaq/homes.html www.epa.gov www.epa.gov/oarhome.html www.epa.gov/CSO.html These are some of the Web sites available on World Wide Web for the US Environmental Protection Agency (EPA). In the IAQ web site, one can find such things as EPA documents, database and the online results from the building assessment survey and evaluation program. The main EPA home page provides links to other EPA sites, including regions throughout the US.

One of the EPA sites also lets you find the information on employees using a search facility. The results include their mail addresses, phone numbers, and e-mail addresses. This is an important feature when trying to contact a specific person.

#### Web Site: www.cmhc-schl.gc.ca

www.cmhc-schl.gc.ca/Research/IEWG/discuss.html Canada Mortgage and Housing Corp. (CMHC) maintains this site. CMHC is active in investigating the indoor environment. The agency is doing valuable work on the presence of mold and how that affects the indoor environment, among other related issues.

CMHC also maintains a discussion page where indoor air environment professionals can post questions and receives comments from CMHC.

#### Web Site: eande.lbl.gov/IEP/

This Web site describes the activities in indoor air environment program at Lawrence Berkeley National Laboratory (LBNL).

#### Web Site: eande.lbl.gov/CBS/NEWSLETTER/CBSNEWS.html

The Web site lists research programs and contains online editions of the center's quarterly newsletter. The Center for Building Science (CBS) at Lawrence Berkeley National Laboratory (LBNL) conducts extensive research on indoor air quality, buildings, and energy issues.

#### Web Site:occ-env-med.mc.duke.edu/oem/wutsnew.htm

This is a very interesting site and provides up-to-date information on "what is globally new in occupational & environmental health". The site provides links to recently released material by the worldwide agencies active in occupational and environmental health (EPA, NIOSH, FDA,CDC, WHO, MSHA, ATSDR, GAO, EID and more). The site is maintained by Dulk's OEM webmaster.

#### Web Site: www.boma.org

Building Owners and Managers Association (BOMA) maintains the site. BOMA is an international organization for those who own and operate buildings. The group sponsors some research that sometimes touches on indoor air quality. The Web site can lead viewers to some of its research activities and more information about the organization.

#### Web Site:www.cutter.com/ewwe/

If anyone seeking European communities' information or activities related to indoor air environment, this is a must-see Web site. The site is maintained by Environmental Watch: Western Europe and provides links to numerous environmental organizations both governmental and non-governmental agencies in European communities countries.

#### Web Site:www.nist.gov

National Institute of standards and Technology (NIST) conducts numerous research projects of interest to the indoor air environment community. The Web site provides details on various projects dealing with how buildings perform- and what this means for the indoor environment.

#### Web Site: www.invent.hut.fi/index.html

The site is maintained by Finnish Ventilation Industry. The Web site provides an overview of the "Industrial Ventilation Development Program (INVENT)" developed by the Finnish ventilation industry and Finnish research/educational institutes. The information on industrial air quality, industrial air technology design, guide books and current research projects related to indoor air environment could be viewed on this site. The summary of reports and current issues related to industrial ventilation can be obtained from this Web site also.

#### CONCLUSION

This paper presents a guide for 44 useful sites for indoor air quality activities. The sites are grouped into services and products, and training/courses, technical organizations, government sites and publications categories. It is hoped that you will find these sites useful for your work.

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# **Air Pollution Control Cost Indexes**

# Update #2

#### William M. Vatavuk, P.E.

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The article "Escalating Air Pollution Control Equipment Costs" [Environmental Progress, 16, pp.S15-S18 (Summer 1997)] introduced the quarterly Vatavuk Air Pollution Control Cost Indexes (VAPCCI) and described how they can be used to adjust air pollution control equipment prices from one date to another. This article also presented equipment size-specific VAPCCI's for nine types of control devices, from first quarter 1996 through fourth quarter 1996 (preliminary) and first quarter 1997 (preliminary). Average VAPCCIs for the years 1994 and 1995 were also listed for these nine devices, plus two more: fabric filters and mechanical collectors. The first update of the VAPCCI, which appeared in our Fall 1997 issue, presented indexes through first quarter 1997 (final) and second quarter 1997 (preliminary).

This update, the second, presents final VAPCCI data for first quarter 1997 (Table 1) and preliminary indexes for third quarter 1997 (Table 3). For convenience, preliminary second quarter 1997 VAPCCI (Table 2) are also included. (The Table 2 VAPCCI is reprinted from the Fall 1997 article.) Finally, an "Indexes Summary" (Table 4) lists the average VAPCCI for the nine control devices, fabric filters, and mechanical collectors. Future VAPCCI updates will appear in upcoming issues.

#### Table 1. Control Device Equipment Cost Indexes: First Quarter 1997 (Final)

Control Device			Equipmen (First Quarte	t Cost Index r 1994 = 100.00	)
	Small	Medium	Large	Average <sup>1</sup>	Range/ Average x 100% <sup>2</sup>
Carbon adsorbers	104.22	104.81	104.65	104.56	12.9
Catalytic incinerators	106.01	105.56	105.10	105.56	16.3
Electrostatic precipitators	109.00	108.57	109.44	109.01	9.7
Flares	105.96	105.56	105.39	105.63	10.1
Gas absorbers	107.10	107.51	107.14	107.25	5.7
Refrigeration systems	105.22	105.33	105.54	105.36	6.0
Regenerative thermal					
oxidizers	107.28	107.69	107.58	107.51	5.5
Thermal incinerators	108.88	108.94	109.19	109.00	3.4
Wet scrubbers	108.33	108.79	108.58	108.57	5.4

<sup>1</sup>Arithmetic averages of the three ECI values.

<sup>2</sup>Calculated as follows:

R/A = {(High Index-Low Index)/|Average index-100|} x 100%

Control Device			Equipment Co	ost Index	
			(First Quarter 19	94 = 100.00)	
	Small	Medium	Large	Average <sup>1</sup>	Range/ Average x 100% <sup>2</sup>
Carbon adsorbers	105.54	106.02	105.89	105.82	8.2
Catalytic incinerators	108.03	107.99	107.84	107.95	2.4
Electrostatic precipitators	108.26	106.91	107.27	107.48	18.0
Flares	107.31	106.99	106.84	107.05	6.7
Gas absorbers	107.45	107.83	107.50	107.59	5.0
Refrigeration systems	106.08	106.20	106.36	106.21	4.5
Regenerative thermal					
oxidizers	107.46	107.86	107.78	107.70	5.2
Thermal incinerators	109.31	109.37	109.58	109.42	2.9
Wet scrubbers	109.13	109.68	109.57	109.46	5.8

#### Table 2. Control Device Equipment Cost Indexes: Second Quarter 1997 (Preliminary)

<sup>1</sup>Arithmetic averages of the three ECI values.

<sup>2</sup>Calculated as follows:

R/A = {(High Index-Low Index)/|Average index-100|} x 100%

#### Table 3. Control Device Equipment Cost Indexes: Third Quarter 1997 (Preliminary)

Control Device			Equipment C (First Quarter 19	ost Index 94 = 100.00)	
	Small	Medium	Large	Average <sup>1</sup>	Range/ Average x 100% <sup>2</sup>
Carbon adsorbers	105.28	105.50	105.33	105.37	4.1
Catalytic incinerators	108.97	109.03	108.96	108.99	0.8
Electrostatic precipitators	109.28	108.69	109.16	109.04	6.5
Flares	107.57	107.16	106.95	107.22	8.6
Gas absorbers	107.58	108.02	107.66	107.76	5.7
Refrigeration systems	106.52	106.65	106.72	106.63	3.0
Regenerative thermal					
oxidizers	107.77	108.13	108.06	107.99	4.5
Thermal incinerators	109.46	109.52	109.60	109.52	1.5
Wet scrubbers	109.56	110.06	109.82	109.81	5.1

<sup>1</sup>Arithmetic averages of the three ECI values.

<sup>2</sup> Calculated as follows:

R/A = {(High Index-Low Index)/|Average index-100|} x 100%

#### Table 4. Indexes Summary

		Vatavuk	Air Pollu	tion Con	trol Cost	Indexes		
			(1st qua	rter 1994	i = 100.0	)1		
Control Device	1995	1st Q	2nd Q	3rd Q	4th Q	1st Q	2nd Q	3rd Q
	Avg.	<b>'</b> 96	<b>'</b> 96	<b>'</b> 96	'96	<b>'</b> 97	<b>'</b> 97 <sup>2</sup>	<b>'</b> 97 <sup>2</sup>
Carbon adsorbers	110.7	109.2	107.5	105.2	103.5	104.6	105.8	105.4
Catalytic incinerators	107.1	107.7	107.0	107.1	106.0	105.6	108.0	109.0
Electrostatic precipitators	108.2	107.0	107.6	108.9	108.4	109.0	107.5	109.0
Fabric Filters <sup>3</sup>	102.7	104.0	104.2	104.8	104.9	105.2	105.4	106.6
Flares	107.5	104.5	104.9	105.1	105.2	105.6	107.1	107.2
Gas absorbers	105.6	108.6	108.2	107.1	107.1	107.3	107.6	107.8
Mechanical Collectors <sup>3</sup>	103.0	103.3	103.3	103.3	103.3	103.5	103.6	103.8
Refrigeration systems	103.0	104.2	104.2	104.4	104.8	105.4	106.2	106.6
Regenerative thermal oxidizers	104.4	105.8	106.0	106.7	106.6	107.5	107.7	108.0
Thermal incinerators	105.9	108.0	108.0	108.3	108.3	109.0	109.4	109.5
Wet scrubbers	112.5	111.7	110.1	109.3	108.0	108.6	109.5	109.8

<sup>1</sup>Index values have been rounded to the nearest tenth.

<sup>2</sup>All second and third quarter 1997 indexes are preliminary.

<sup>3</sup>For fabric filters and mechanical collectors, each quarterly value shown is the average of the Producer Price Indexes for the three months in question, divided by the average of the PPI's for January, February, and March 1994 (i.e., first quarter 1994).

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# Estimating Physical Properties for Control Equipment Design

#### Douglas A. Logan

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There is a great deal of information about physical properties available to engineers. The trick is in knowing where to find what is needed when it is needed. Many of the widely available sources lack information that is needed for process design. Material Safety Data Sheets (MSDSs) include relatively little physical properties data and no transport properties. Standard references like Perry's Chemical Engineer's Handbook, the CRC Handbook of Chemistry and Physics, and Lange's Handbook of Chemistry may not have data for a particular property or compound.

The handbooks have information about hydrocarbons, and some of the common industrial alcohols, ketones, and esters. Data on some common industrial solvents, such as the glycol ethers and their acetates, is rather sketchy in the classic manuals. What can an engineer do if there is a need for data not available in the common references?

For example, USEPA published several guidance manuals that present cost estimating techniques for air pollution control equipment. Engineers working in industry and for regulatory agencies apply the guidance in these manuals in trying to determine whether any of several control options represent the Best Available Control Technology (BACT) for an emissions source. BACT is the maximum level of control, considering economic factors as well as pollutant removal.

Even the simplified design procedures in USEPA's Control Technology for Hazardous Air Pollutants require information that is just not found on an MSDS. Incinerator operating cost estimates depend on the beat available from the pollutants, the beat of combustion. The sizing and cost estimating procedure for refrigerated condensers calls for vapor pressure data, the beat of vaporization, and the beat capacity (specific beat). A cost estimate for an absorption system to scrub air pollutants demands vapor-liquid equilibrium information, diffusivities, and the pollutant molar volume.

Instead of starting a game of phone tag with the vendor's customer service department or spending several bundred dollars for a reference book you may not need again for five years, why not try estimating techniques for physical properties? These techniques bave been around for a long time and offer reasonable accuracy within their limits. Estimated values are certainly accurate enough for budgetary-quote-level design procedures. More accurate estimating techniques are available [3]. The drawback to more sophisticated methods is increased complexity. Often, the more precise estimate calls for a multi-step calculation, with several adjustable parameters. The methods described here are fairly simple, either empirical formulas or group contribution schemes.

#### **HEAT OF COMBUSTION**

In estimating the operating cost of a fume incinerator, it is essential to know the contribution that the pollutant stream makes to combustion. The heat of combustion is relatively easy to estimate using the method of Verma and Doraiswamy, simply add up the contribution of various groups shown in Table 1 and subtract the heat of formation of the CO<sub>2</sub> and H<sub>2</sub>O formed [5]. Unfortunately, group contribution methods require a good bit of chemistry knowledge—not for the adding and subtracting, but for recognizing the groups in the pollutant molecules and the stoichiometry of the combustion reaction. For example, consider the common industrial solvent, 2-butoxyethanol (ethylene glycol monobutyl ether, or butyl cellosolve). The structural formula is:

$$CH_2OH - CH_2 - O - CH_2 - CH_2 - CH_2 - CH_3$$

and the group contributions to the heat of formation for 2butoxyethanol in the ideal gas state are:

Group	Number	$\Delta H_f$ (kcal/g mole)	Contribution (kcal/g mole)
- CH <sub>3</sub>	1	10.25	10.25
$-CH_{2}^{-}$ -OH	5	- 4.94	-24.7
(primary alcohol)	1	-41.2	-41.2
-0-	1	-24.2	-24.2
Heat of formation			-80

We can find the heat of combustion from the heat of formation by subtracting the heats of formation for the reaction products, carbon dioxide and water. The combustion reaction for 2-butoxyethanol in the gas phase is:

$$C_6H_{14}O_2 + 8.5O_2 \rightarrow 6CO_2 + 7H_2O_2$$

TABLE 1. C	Group Contributions	o Heat of Formation	
	$\Delta H_f$		$\Delta H_f$
Group	(kcal/g mole)	Group	(kcal/g mole)
Non-ring increments		Cycloalkane ring corrections	
$-CH_3$	10.25	3-member	24.13
- CH <sub>2</sub> -	-4.94	4-member	18.45
> CH -	-1.29	5-member	5.44
> C <	0.62	6-member	-0.76
$-CH = CH_2$	15.02	Halogen-containing groups	
$> C = CH_2$	20.5	- F	-45.1
-CH = CH - (cis)	17.96	- Cl (1st or 2nd)	-8.25
-CH = CH - (trans)	17.83	Oxygen-containing groups	
= CH -	-20.1	-OH (primary)	-41.2
> C = C <	- 30.46	– OH (secondary)	-43.8
≡ CH	27.1	-OH (tertiary)	- 47.6
≡ C	27.38	– OH (aromatic)	- 45.1
Branching in alkanes		-0-	-24.2
side chain with 2 or more carbon atoms	0.8	> C = O	-31.48
3 adjacent > CH—groups	-1.2	-CH = O (aldehyde)	-29.71
adjacent $> C < and > CH - groups$	0.6	– COOH (acid)	-94.68
2  adjacent > C <  groups	5.4	—COO— (ester)	- 79.8
Nitrogen-containing groups		Branching in aromatics	
$-C \equiv N$	36.82	Double branching	
-N = C <	44.4	1,2 position	0.94
$-NO_2$	-7.94	1,3 position	0.58
$-NH_2$ (aliphatic)	3.21	1,4 position	0.58
- NH <sub>2</sub> (aromatic)	-1.27		
> NH – (aliphatic)	13.47	Triple branching	
> NH – (aromatic)	8.5	1,2,3 position	1.8
> N – (aliphatic)	18.94	1,2,4 position	0.44
> N - (aromatic)	8.5	1,3,5 position	0.44

The heats of formation for  $CO_2$  and water vapor are -94kcal/g mole and -58 kcal/g mole, respectively, the heat of formation for elements like oxygen (O2) is zero. Multiplying each contribution by the stoichiometric coefficient and summing algebraically (pay attention to the signs and be sure to subtract the product side from the reactant side) gives a heat of combustion for 2-butoxyethanol of 890 kcal/g mole or 7.5 kcal/g (13,600 BTU/lb.)

#### VAPOR PRESSURE

It seems that reference books offer more information about vapor pressure than for any other physical property. Perry's Handbook includes an alphabetical table of vapor pressure data. The author's rather aged copy of the CRC Handbook has a table arranged by empirical formula. A recent edition of Lange's Handbook offers a table of constants for vapor pressure-temperature correlations, either the Antoine equation or the Clausius-Clapeyron equation discussed below.

Chemical engineering students learn to apply the Clausius-Clapeyron relationship (Eq. 1) at about the sophomore level. If all that is needed is to interpolate a value somewhere in the ranges covered by tabulated data in the CRC Handbook or Perry's, the Clausius-Clapeyron equation is enough. However, even if the particular compound of interest can not be found in one of these references, material safety data sheets often provide two data points for vapor pressure, the atmospheric boiling point (the temperature where p = 760 mm Hg) and one other value, typically the vapor pressure at 20°C.

$$\ln p = A - \frac{B}{T} \tag{1}$$

where

p = vapor pressureT = absolute temperature

A, B = constants

Engineers can use vapor pressure data from the MSDS to solve Eq. 1 for the constants and then determine vapor pressures at different temperatures. There is one very serious caution here-although Eq. 1 is based on an exact thermodynamic relationship, the equation is not rigorous. Using Eq. 1 to extrapolate or to interpolate over a wide range may lead to significant errors.

With data from two points the constants are:

$$B = \frac{T_1 \ T_2 \ (\ln \ p_1 - \ln \ p_2)}{(T_1 - T_2)} \tag{2}$$

and

$$A = \ln p_1 + \frac{B}{T_1} \tag{3}$$

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For the sample compound used above, 2-butoxyethanol, the atmospheric boiling point is  $171^{\circ}C$  (444 K), and the vapor pressure given on an MSDS is 0.88 mmHg at 25°C (298 K). Substituting these values into Eqs. 2 and 3:

$$B = \frac{(298)(444)(\ln 0.88 - \ln 760)}{(298 - 444)} = 6,130 \text{ K}$$

and

$$A = \ln \left( 0.88 \right) + \frac{6,130}{298} = 20.4$$

A user would have to be rather desperate to apply the Clausius-Clapeyron technique over such a wide temperature range, it is included here because it is the simplest correlation available, and because vapor pressure information is probably the easiest of any physical properties data to find in manuals. More rigorous estimating methods that require only one vapor pressure value are available. For example, Riedel's method uses the critical temperature, critical pressure, and boiling point [5]. Still other methods use the heat of vaporization and compressibility factor [3].

#### HEAT OF VAPORIZATION

A number of estimating methods for the heat of vaporization start with the Clausius-Clapeyron relationship. The methods vary mainly in their handling of the difference in vapor and liquid phase molar volumes that appear in the Clapeyron equation. One of the simplest to use is the Giacolone equation (Eq. 4) that treats the difference in vapor and liquid compressibilities (another way of expressing the difference in molar volumes) as 1 [3].

$$\Delta H_{\rm vap} = RT_b \ln\left(P_c\right) / (1 - T_b/T_c) \tag{4}$$

where

$$\Delta H_{vap}$$
 = heat of vaporization, cal/g-mole  
 $T_b$  = normal boiling point, K  
 $P_c$  = critical pressure, atm  
 $T_c$  = critical temperature, K  
 $R$  = gas law constant. 1.9872 cal/g-mole F

Readers will of course notice that Eq. 4 involves two critical properties, values that may also be difficult to find in the literature. However, the critical temperature and critical pressure are quite easy to estimate, using Lydersen's group contribution methods, Eqs. 5 and 6 [3,5].

$$T_c = \frac{T_b}{0.567 + \Sigma \Delta T - (\Sigma \Delta T)^2}$$
(5)

where

 $T_c$  = critical temperature, K

 $T_b$  = normal boiling point, K

 $\sum \Delta T = \text{sum of critical temperature increments from Table}$ 

$$P_c = \frac{M}{\left(0.34 + \Sigma \Delta P\right)^2} \tag{6}$$

where

 $P_c$  = critical pressure, atm

M = molecular weight, g/g mole

 $\Sigma \Delta P =$  sum of critical pressure increments from Table 2

TABLE 2. Critical Property Increments					
Group	$\Delta T$	$\Delta P$	Group	$\Delta T$	$\Delta P$
Non-ring increments			Oxygen increments		
-CH <sub>3</sub>	0.020	0.227	– OH (alcohols)	0.082	0.060
$-CH_2^2$	0.020	0.227	– OH (phenols)	0.031	-0.020
> CH –	0.012	0.210	-O - (non-ring)	0.021	0.160
> C <	0	0.210	-O - (ring)	0.014	0.120
$= CH_2$	0.018	0.198	> C = O (non-ring)	0.040	0.290
= CH -	0.018	0.198	> C = O (ring)	0.033	0.200
= C <	0	0.198	-CH = O (aldehyde)	0.048	0.330
= C =	0	0.198	- COOH (acid)	0.085	0.400
≡ CH	0.005	0.153	-COO - (ester)	0.047	0.470
≡ C	0.005	0.153	= O (except as above)	0.020	0.120
Ring increments			Nitrogen increments		
-CH <sub>2</sub> -	0.013	0.184	$-NH_2$	0.031	0.095
> CH -	0.012	0.192	> NH (non-ring)	0.031	0.135
> C <	-0.007	0.154	> NH (ring)	0.024	0.090
= CH -	0.011	0.154	> N - (non-ring)	0.014	0.170
= C <	0.011	0.154	> N- (ring)	0.007	0.130
= C =	0.011	0.154	$-C \equiv N$	0.060	0.360
Halogen increments			$-NO_2$	0.055	0.420
-F	0.018	0.224	Sulfur increments		
-Cl	0.017	0.320	– SH	0.015	0.270
- Br	0.010	0.50	-S - (non-ring)	0.015	0.270
-I	0.012	0.83	-S - (ring)	0.008	0.240
			= S	0.003	0.240

For the sample compound, 2-butoxyethanol,

Group	Number	Critical temperature increment	Critical temperature contribution	Critical pressure increment	Critical pressure contribution
- CH <sub>3</sub>	1	0.020	0.020	0.227	0.227
$-CH_{2}$ -	5	0.020	0.100	0.227	1.135
-OH	1	0.082	0.082	0.060	0.060
-0-	1	0.021	0.021	0.160	0.160
Total		$\Sigma \Delta T =$	0.223	$\Sigma \Delta P =$	1.582

Substituting into Eqs. 5, 6, and 4

$$T_{c} = T_{b} / (0.567 + \Sigma \Delta T - (\Sigma \Delta T)^{2})$$
  
= 444/(0.567 + 0.223 - (0.223)^{2}) = 600 K  
$$P_{c} = M / (0.34 + \Sigma \Delta P)^{2} = 118 / (0.34 + 1.582)^{2} = 42 \text{ atm}$$
  
$$\Delta H_{vap} = RT_{b} \ln (P_{c}) / (1 - T_{b} / T_{c}) = (1.9872)(444)$$
  
$$\times (\ln(42)) / (1 - 444/600) = 12,700 \text{ cal/g mole}$$

#### LOWER EXPLOSIVE LIMIT

The lower explosive limit (LEL) is a factor in designing pollution control systems for flammable vapors. Typically, a stream containing more than 25% of the LEL requires explosion proof electrical equipment. Engineers can calculate the LEL from the flash point temperatures, a simple vapor pressure-temperature relationship, like the Clausius-Clapeyron equation discussed above or the Antoine equation, and a vapor pressure-concentration relationship like Raoult's Law (Eq. 7).

$$y_i = p_i / P \tag{7}$$

where

 $p_i$  = vapor pressure P = total pressure

The flash point and LEL are generally found on an MSDS. However, if the information is not available, there are correlations for estimating the flash points of several classes of organic compounds [3]. The correlations are all of the form shown in Eqn. 8:

$$t_f = K_1 t_b - K_2 \tag{8}$$

where

 $t_f$  = flash point temperature, °F  $t_b$  = atmospheric boiling point, °F  $K_1$ ,  $K_2$  = empirical constants from Table 3

For the example compound, 2-butoxyethanol, the Hagopian "alcohols" correlation seems to be the best choice. Substituting the boiling point of 340°F (171 °C) and the appropriate constants into Eq. 8, we find that:

$$t_f = 0.7056 (340) - 77.1 = 163^{\circ}F$$

This result does not compare very well to the published value, 143°F (14% error) [1]. However, to continue the example, the LEL is the equilibrium concentration at the flash point. The user can determine the vapor pressure at the flash point and then apply Raoult's Law (Eq. 7) to find the concentration.

From the earlier example

$$\ln p_i = 20.4 - 6,130/T = 20.4 - 6,130/346 = 2.68$$
$$p_i = \exp(2.68) = 14.6 \text{ mm Hg}$$
$$v_i = 14.6/760 = 1.9\%$$

NFPA 325M - 1984 lists an LEL for 2-butoxyethanol of 1.1% at  $200^{\circ}F^{1}$ .

		Boiling point			Average
Compound type	Method	range (°F)	<i>K</i> <sub>1</sub>	<i>K</i> <sub>2</sub>	deviation (°F)
Hydrocarbons <sup>1</sup>	PM closed cup	150-550	0.683	119	14
Alcohols <sup>2</sup>	closed cup	180-491	0.7056	77.1	6.7
Aldehydes <sup>2</sup>	closed cup	69-329	0.6901	92.3	6.9
Amines <sup>2</sup>	closed cup	120-531	0.7962	120.9	17
Ketones <sup>2</sup>	closed cup	133-433	0.6717	95.2	8.0

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TABLE 4. Group Contributions for Molar Liquid Heat Capacity			
Group	Value (cal/g mole K)	Group	Value (cal/g mole K)
- CH <sub>3</sub>	8.80	-0-	8.4
$-CH_{2}^{-}$	7.26	> C = O	12.66
> CH -	5.00	-CH = O	12.66
>C<	1.76	-COOH	19.1
$= CH_2$	5.20	-coo -	14.5
= CH -	5.10	-CH <sub>2</sub> OH	17.5
= C <	3.80	> CHOH	18.2
≡ CH	5.90	> COH -	26.6
≡ C	5.90	-OH	10.7
> CH - (ring)	4.4	$-ONO_2$	28.5
= C < or > C < (ring)	2.9	$-NH_2$	14.0
$-CH_{2}-$ (ring)	6.2	- NH -	10.5
- CL (1st or 2nd on a carbon)	8.6	-N = (ring)	4.5
-F	4.0	$-C \equiv N$	13.9

Note: Add 4.5 for any carbon group joined by a single bond to a carbon group connected by a double or triple bond to a 3rd carbon group. In some cases, a carbon group will meet this criterion in more than one way, add 4.5 for each time a group fills the criterion. There are 3 exceptions to the addition rule: 1. Do not add 4.5 for a – CH<sub>3</sub> group. 2. For a – CH<sub>2</sub>– group, add 2.5 for the first time it meets the addition criterion and 4.5 for each further case.

3. Do not add anything for carbon groups in a ring.

The LEL estimate is highly dependent on the vapor pressure value. For comparison, Riedel's vapor pressure correlation, mentioned earlier, returns a value of 7 mm Hg at the estimated flash point, corresponding to an LEL of 0.9%. Note that for the simple purpose of determining whether an electrical installation requires explosion proof equipment, underestimating the LEL errs on the side of safety.

#### LIQUID HEAT CAPACITY

Chueh and Swanson developed a useful group contribution method for determining the molar liquid heat capacity at 25°C [3,5]. Liquid heat capacity of a volatile pollutant is needed to determine the sensible heat load on a condenser system used for pollution control. Table 4 shows the contributions of various functional groups to heat capacity. This method reportedly gives good results if the critical temperature of the compound is greater than 390 K [5]. Other estimating methods for heat capacity typically require critical property values [3, 5].

For the example case:

Group	Number	Value (cal/g mole K)	Contribution (cal/g mole K)
-CH <sub>3</sub>	1	8.8	8.8
$-CH_{2}$	5	7.26	36.3
-OH	1	10.7	10.7
-0-	1	8.4	8.4
Molar heat			
capacity			64.2

Dividing by the molecular weight gives  $C_p$  in mass units, 0.54 cal/gK (BTU/lb °R).

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#### GAS PHASE DIFFUSION COEFFICIENTS

The absorption design technique described in USEPA's BACT guidance calls for both gas and liquid phase diffusion coefficients (or diffusivities). The simplest way to estimate the gas phase property is the method of Fuller, Schettler, and Giddings, Eq. 9 [5]. This method gives values within 5 to 10% of experimental results.

$$\mathfrak{D}_{AB} = 10^{-3} T^{1.75} \frac{\left(\frac{M_A + M_B}{M_A M_B}\right)^{0.5}}{P\left((\Sigma v)_A^{0.33} + (\Sigma v)_B^{0.33}\right)^2} \qquad (9)$$

where

 $\mathfrak{D}_{AB}$  = diffusion coefficient, cm<sup>2</sup>/sec T = absolute temperature, K P =pressure, atm  $M_A$ ,  $M_B$  = molecular weights

 $(\Sigma v)_A$ ,  $(\Sigma V)_B$  = atomic diffusion volumes from Table 5

For the sample compound used earlier, 2-butoxyethanol, let "B" represent air, so  $(\Sigma v)_B = 20.1$  from Table 5 and  $M_B$ 

Atomic	and structu	aral diffusion volume inc	crements
С	16.5	Cl	19.5
Н	1.98	S	17.0
0	5.48	Aromatic ring	-20.2
N	5.69	Heterocyclic ring	-20.2
D	iffusion vol	umes for simple molecu	ules
air	20.1	CO <sub>2</sub>	26.9
CO	18.9	NH <sub>3</sub>	14.9
H <sub>2</sub> O	12.7	CCl <sub>2</sub> F <sub>2</sub>	114.8

= 29. The molecular weight of 2-butoxyethanol  $(M_A)$  is 118, and  $(\Sigma v)_A$  is found from data in Table 5.

Group	Number	Structural increment	Contribution
С	6	16.5	99
н	14	1.98	27.72
0	2	5.48	10.96
$(\Sigma v)_A$			138

Substituting values into Eq. 9 and letting P = 1 atm:

$$\mathfrak{D}_{AB} = 10^{-3} (298)^{1.75} \frac{\left(\frac{118+29}{(118)(29)}\right)^{0.5}}{1\left((138)^{0.33} + (20.1)^{0.33}\right)^2} = 0.071 \frac{\mathrm{cm}^2}{\mathrm{sec}}$$

#### MOLAR VOLUME

Schroeder developed a very simple structural contribution method, shown in Table 6, for determining liquid molar volume at the normal boiling point with an average error of 3.4% [3]. The design procedure for absorption systems in USEPA guidance manuals requires the pollutant molar volume, not explicitly, but for determining the liquid phase diffusivity. Diffusivities appear in the liquid- and gas-phase Schmidt number that help determine the height of a transfer unit.

TABLE 6. Structural Contributions to Liquia Molar Volume			
Structural Feature	Increment (cm <sup>3</sup> /g mole)	Structural Feature	Increment (cm <sup>3</sup> /g mole)
С	7	I	38.5
н	7	S	21
N	7	Rings	-7
0	7	C – C bond	0
Br	31.5	C = C bond	7
Cl	24.5	$C \equiv C \text{ bond}$	14
F	10.5		

For the sample compound used above, 2-butoxyethanol,

Species	Number	Atomic volume	Contribution
С	6	7	42
н	14	7	98
0	2	7	14
Molar volume (cm <sup>3</sup> /g mole)			154

For comparison, another structural contribution method for molar volume at the normal boiling point, that of LeBas, returns a value of  $159 \text{ cm}^3/\text{g}$  mole for 2-butoxyethanol [4].

#### LIQUID PHASE DIFFUSIVITY

The liquid phase diffusivity of a pollutant in a solvent also appears in the USEPA design procedure for absorption systems. The Wilke-Chang method (Eq. 10) is the simplest method for estimating this property [3, 5]. The method is suited for dilute solutions of A in B, with an error of about 10% [5].

$$\mathfrak{D}_{AB}^{0} = 7.4 \times 10^{-8} \frac{\left(\varphi_{B} M_{B}\right)^{0.5} T}{\mu_{B} V_{A}^{0.6}}$$
(10)

where

 $\mathfrak{D}_{AB}^0$  = liquid phase diffusivity, cm<sup>2</sup>/sec

- $\varphi_b$  = association parameter for the solvent, 2.6 for water
- $M_B$  = molecular weight of the solvent
  - T = absolute temperature, K
- $\mu_B$  = solvent viscosity, cP
- $V_A$  = solute molar volume, cm<sup>3</sup>/g mole

If the solvent is water a common choice in air pollution control scrubbers, Eq. 10 reduces to:

$$\mathfrak{D}_{AB}^{0} = 5.06 \times 10^{-7} \frac{T}{\mu_{B} V_{A}^{0.6}} \tag{11}$$

For the example compound 2-butoxyethanol, in water at 25°C:

$$\mathfrak{D}_{AB}^{0} = 5.06 \times 10^{-7} \frac{(298)}{(0.8904)(154)^{0.6}} = 8.2 \times 10^{-6} \frac{cm^{2}}{sec}$$

In this example, the viscosity of water is taken from the NBS (now NIST) correlation [6].

#### VAPOR LIQUID EQUILIBRIUM

The vapor-liquid equilibrium relationship is essential for processes like air stripping and absorption. Henry's Law (Eq. 12) is the simplest vapor-liquid relationship for dilute mixtures, useful for the simple design calculations involved in air stripping and scrubbing processes. The low temperatures, pressures, and concentrations found in most pollution control situations are suited to a less rigorous approach like Henry's Law. The question then is where to find Henry's Law constants.

$$p_i = HX_i \tag{12}$$

where

 $p_i$  = partial pressure of *i* in the vapor phase, atm

 $x_i$  = mole fraction of *i* in the liquid phase

H = Henry's Law constant, atm/(mole fraction)

The engineer can calculate the Henry's Law constant easily from vapor pressure and solubility data by rearranging Eq. 12 into Eq. 13.

$$H = \frac{p_{\text{vap}}}{S} \tag{13}$$

	TABLE 7. Structural Contributions to Activity Coefficient					
Species	Bonded to	Contribution to ln γ	Species	Bonded to	Contribution to ln γ	
CH <sub>3</sub>		-1.43	C = O	alkyl	9.3	
CH <sub>2</sub>	2 alkyl C	-0.35	-0-	alkyl	6.8	
CH	3 alkyl C	0.55	CH <sub>2</sub> Cl	alkyl C	2.4	
CH <sub>2</sub>	1 alkyl C and 1 O	-0.30	CHO	CorO	7.4	
CH	2 alkyl C and 1 O	0.28	-0-	carboxylic acid or ester	-1.22	
OH	alkyl C	10.3				
C = 0	carboxylic acid or ester	9.4	Distant po ethylene g	blar interaction for glycol ethers	- 3.64	

where

 $p_{vap} = vapor \text{ pressure of } i$ S = solubility

However, Eq. 13 is only useful if solubility data are readily available. Quantitative information about solubility is notably sketchy in the handbooks. Although there are estimating techniques for solubility, using one may require estimating yet another property, like the octanol-water partition coefficient. A single step method better suits the preliminary design-level situation discussed here.

Hine and Mookerjee presented a group contribution method for what they call an "activity coefficient,"  $\gamma$  [2]. The researchers actually provide a correlation for the inverse of the Henry's Law constant defined in Eq. 12. Their method involves summing group contributions to the logarithm of  $\gamma$ . Table 7 is an abridged version of the Henry's Law constant correlation, converted to natural logarithms.

The Hine and Mookerjee activity coefficient is the ratio of the liquid phase concentration to the vapor phase concentration. If we assume a dilute water solution as the liquid phase and ideal gas behavior in the vapor phase, then Eq. 12 reduces to Eq. 14, and the Henry's Law constant is:

$$\gamma = \frac{C_w}{C_g} \tag{14}$$

However,

$$C_w = \frac{N_i}{V} = \frac{x_i N}{V} = \frac{x_i \rho}{M} = 55.5 x_i$$
(15)

and

$$C_g = \frac{n_i}{V} = \frac{p_i n}{pV} = \frac{p_i}{RT}$$
(16)

Substituting Eqs. 12, 15, and 16 into Eq. 14:

$$\gamma = \frac{55.5 x_i}{\frac{p_i}{RT}}$$
$$H = \frac{p_i}{x_i} = \frac{55.5 RT}{\gamma}$$

and at 298 K (25°C)

$$H = \frac{1,357}{\gamma} \tag{17}$$

For our faithful example compound, 2-butoxyethanol

Group	Number	Group Contribution	Contribution
CH <sub>3</sub> -	1	-1.43	-1.43
CH <sub>2</sub> ,			
bonded to 2 alkyl C	2	-0.35	-0.70
CH <sub>2</sub> ,			
bonded to 1 alkyl C	3	-0.30	-0.90
and 1 O			
OH, alkyl	1	10.25	10.25
—O—, ether	1	6.75	6.75
distant			
polar interaction	1	-3.64	-3.64
ln γ			10.33
γ			30,600

Inserting the value of  $\gamma$  into Eq. 17, H = 0.044 atm/(mole fraction solute in liquid) at 298 K.

#### CONCLUSIONS

Physical property data are widely available to those who need it. Various reference manuals and technical articles offer sources. There are certainly many engineers whose need for physical properties data is very infrequent, too rare to justify investing in a library of reference books. When high precision is unnecessary, the occasional need for information not tabulated in the common references can be satisfied with these estimating techniques. More sophisticated estimates are also available, often involving critical properties, activity coefficients, and other thermodynamic properties.

Even as the number of information sources expands, older chemical engineering methods retain their usefulness. If a reader chooses not to preserve this article, Perry's Handbook describes estimating methods for every property described here except flash point and the Henry's Law constant. Engineering is often an exercise in optimization and the principle can apply to the engineer's time and expense budget as well as the project. If the circumstances allow use of estimated properties, remember that the methods are available and suitable for many applications.

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# Application of Design for Environment Concepts to the Semiconductor Industry

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Motorola has traditionally focused on cost, yield, performance, and logistics as primary drivers for decision-making. In the semiconductor industry, environmental issues have resulted in major modifications of tools and process steps because they are not routinely considered when making process design and manufacturing choices, nor is their impact on cost, yield, and cycle time. Certain business driving forces, such as cost, sustainability of processes/tools, time to market, market access, and market share, are leading Motorola to a cultural change in which environmental impacts must be considered during product and process design; however, design and process engineers have not been able to adequately address these impacts. Motorola's Advanced Process Research and Development Laboratory (APRDL) in the Semiconductor Product Sector (SPS) has recognized this and has established its own environmental group (separate from the site environmental compliance group) to implement a Design for Environmental (DFE) strategy. This group works with several project teams to address environmental issues in process development. To empower engineers to consider the environmental impacts of their materials and processes at the earliest possible stage, the APRDL environmental group has also developed a DFE training course. This web-based course targets semiconductor design and process engineers and is available through Motorola University, the corporate training institution.

In the broadest terms, DFE is a systematic management approach for evaluating and mitigating environmental concerns at the earliest possible stages of process design or product life cycle. It includes ongoing evaluation during the product life cycle, while optimizing the balance between environmental priorities and factors such as cost, yield, cycle time, performance, etc. This optimization requires that Motorola make value judgments based on the best information available. The course is designed to provide semiconductor engineers with the neccesary background to understand the concepts of DFE and the tools to incorporate consideration for environmental impacts into their daily routine without adding a significant burden to their workload.

#### **BUSINESS DRIVING FORCES**

Motorola SPS recognizes that DFE is about more than a healthy environment and a safe workplace. There are significant business reasons to consider environmental impacts at the earliest possible stages [1].

- Decreasing cost—DFE often results in reduced material consumption, reduced cycle time, reduced regulatory bureaucracy, avoided delays, etc. These all translate into cost savings. DFE reduces operating costs and risks to Motorola by reducing—or eliminating—storage, handling, training-for-use, safe management, site response, compliance requirements, and final disposal of hazardous materials and wastes.
- Achieving sustainability for tools/processes—Early consideration of environmental impacts may help ensure that a tool/process is sustainable for the next technology generation. Or, at least, environmental issues will NOT be the reason that the tool/process cannot be used later.
- Minimizing time to market—Addressing environmental issues in the design and development stages will help avoid costly delays at the implementation stage like permit modifications, environmental reviews, retrofits, etc. Unexpected or unprecedented regulatory changes and limitations on the use of hazardous materials can derail product introduction and new product development. DFE prevents such interruptions by anticipating these potential road-blocks.
- Maintaining market access—Compliance with international standards, like ISO 14000 and EMAS, may become mandatory to conduct business in many countries—especially in Europe. A DFE program is an essential element of these types of standards.
- Increasing market share—environmental performance is now viewed as a distinct competitive tool. Customers may migrate towards companies with proactive environmental programs and environmentally preferable products—particularly in Europe.
- Reducing corporate risk factors—In a era of severe

cost constraints, corporations like Motorola are keen to reduce operating risks to increase stakeholder value. DFE offers many risk reduction opportunities, such as elimination of hazardous waste treatment, storage, and disposal liability; reduction in workplace hazards (safety and hazardous material exposure risks); anticipation of bans or restrictions on critical materials; early identification of required permit modifications; and planning new products with an eye toward eventual product and materials take-back (where a company is required to take back a product or material at the end of its useful life) and similar mandates.

Projecting environmental leadership—Corporations like Motorola now include environmental leadership as one of the core values of business. A DFE program will allow Motorola to continue as a "Best in Class" environmental leader.

#### DFE TOOLS

To enable engineers to consider environmental issues, they must be provided with the tools to evaluate environmental impacts; most process engineers have no environmental background. To develop such tools, the APRDL environmental group started with the DFESH strategy document [1] and DFESH training modules [2] produced by SEMATECH, a research consortium of ten U.S. semiconductor manufacturers. The group also installed the CARRI (Computerized Assessment of Relative Risk Impacts) relative risk assessment software (developed by SEMATECH) which evaluates the EHS risks of materials and their associated semiconductor manufacturing processes. This software is now available from EORM (Environmental Occupational Risk Management) in San Jose, CA. Using these tools, along with DFE and semiconductor processing knowledge from within Motorola [3], a web-based DFE course was developed for semiconductor engineers.

#### **DFE Course Format**

Motorola has developed a self-instructed, computerbased training course for Motorola University which follows the DFE concept: ENG190-"Designers Guide to Clean Process Design." The development team decided to make the course web-based so it would be available to all of SPS. Engineers can access the course through any computer terminal with a web browser (which most engineers have on their personal computer). There is no class to attend-engineers can receive four hours of training credit without leaving their office! This not only saves money in training (eliminates the need for a facilitated course) and time for engineers, but it also increases the likelihood that engineers will take the course. Travel to a Motorola University location is also not required. This course is the first ever web-based course for Motorola University and has set a precendence for more web-based training.

The training course has six sections:

- 2) DFE Design Aid Methodology
- 3) DFE Design Aid
- 4) CARRI: Risk Assessment Model
- 5) Resources and Guidelines
- 6) Application for Training Credit

The rationale sections provides the necessary background for understanding DFE. It explains the business driving forces behind DFE and presents case studies to emphasize the concept of cost savings. The design aid methodology describes the primary tool, or design aid, provided with the course: the process matrix, which is a qualitative set of questions regarding environmental aspects of materials, processes, facilities, and emissions. It gives instructions for using the process matrix, which is described later. The Design Aid is the process matrix itself. The section on CARRI is a description of the complementary risk assessment tool, CARRI-Computerized Assessment of Relative Risk Impacts. This software provides a relative environmental risk evaluation of two or more processes and their associated materials and may be available in a web-based format in 1998. Finally, additional resources and guidelines for reference are provided.

#### **DFE Process Matrix**

The process matrix is a qualitative set of questions (yes/no format) specific for each Tier that assist the engineer in considering environmental, health and safety impacts of his operations. The matrix has environmental, health and safety impact categories as rows and manufacturing process "lifecycle" categories as columns. The categories are identical for each of the Tier matrices. There are four questions in each element; the matrix score is the total number of "yes" answers. The purpose of this score is not to compare to an "acceptable" score, but is rather to point out the areas for improvement in the current process concept. The matrix can also be completed for two or more process options and the scores compared for a relative environmental consideration evaluation.

The four environmental impact categories are as follows: Sustainability-Resource Use; Sustainability-Energy Use; Human Safety and Toxicity; and Eco-Toxicity. The concept of sustainability is generally defined as "...development that meets the needs of the present without compromising the ability of future generations to meet their own needs," or "...future generations must not inherit less environmental capital than the current generation inherited." To meet the criteria of sustainability, the Resource Use category addresses material consumption (including all process materials and natural resources) and reuse/recycle in each of the process "lifecycle" stages. Energy use covers consumption during operations at these stages. Human Safety and Toxicity focuses on the employees and the workplace environment and addresses issues of exposure to people. Eco-Toxicity focuses more on the total environment outside of the lab and hazard to ecosystems and human populations.

There are four categories in the "lifecycle" of the manufacturing process: Consumables and Equipment Sourcing, Process, Tools, and Integration; Facilities, Reuse and Recycle; and Byproducts. Consumables and Equipment Sourcing covers activities associated with the specification, purchase, and delivery of process materials and equipment. Process, Tools, and Integration includes activities associated with the process or tool itself. Facilities, Reuse, and Recycle addresses issues with the lab support operations, such as gas delivery, auxiliary equipment, DI water usage, etc. And recycling or reusing process materials, By-products, Emissions, and Disposal covers post-process activities

<sup>1)</sup> Rationale for DFE

TABLE 1. DFE Process Matrix				
	Consumables and Equipment Sourcing	Process, Tools and Integration	Facilities, Re-use and Recyle	By-products, Emissions and Disposal
Sustainability-Resource Use	????	????	????	????
Sustainability-Energy Use	????	????	????	????
Human Safety and Toxicity	????	????	????	????
Eco-Toxicity	????	????	????	????

-what happens to the process materials in the tool, what by-products are formed, what is emitted from the tool, and subsequently the environment, etc. Table 1 illustrates the process matrix concept.

#### **Course Pilot Testing**

Once the course was developed by the team, it was pilot tested by process and device engineers in APRDL and MRST (Materials Research and Strategic Technology– another R&D group in Motorola SPS). The participants were asked to navigate through the course with minimal guidance provided by the team. They looked at each section and provided feedback. The primary goal of this test was to determine if the course content was appropriate for the target audience, process engineers. The course was also reviewed by Austin environmental and safety staff.

Modifications were made to the course following suggestions from the process engineers and environmental and safety staff. The engineers provided input to make the process matrix questions more applicable to their job function. They also indicated sections that were not clear or did not provide enough explanation based on their limited environmental background. A process flow diagram illustrating the flow of material into and the waste and emissions out of a lab was added. The environmental and safety staff suggested some additions to the process matrix questions based on experiences they have had with process areas. The lessons learned from this initial pilot testing were extremely valuable in making the course successful across SPS.

#### **Course Implementation**

Pilot testing has been completed for the DFE course and the course has been transferred to Motorola University. It resides on the Motorola University Southwest server and is accessible throughout Motorola, though it has particular application for SPS. Links to the course can be found on the Motorola University catalog web page as well as other homepages for individual labs and fabs in SPS. This will ensure widespread knowledge of the course's existence. This is an internal Motorola web and is not accessible outside Motorola.

The Austin sites pollution prevention team will also be using the DFE course as the primary tool to provide the labs to educate them on the concept and to assist them with implementing pollution prevention projects. The team will present the course to the lab engineering managers and encourage them to have their engineers complete it. The development organizations will do the same.

#### **CARRI Software Implementation**

Motorola evaluated the CARRI software developed by SEMATECH and determined that it would be an extremely valuable DFE tool for semiconductor engineers. Some R&D groups in Motorola, including APRDL, have been able to use CARRI on individual computers to conduct risk assessments of materials and their associated processes. The APRDL environmental group has performed several CARRI evaluations and has used the results to influence process development and manufacturing decisions. The results from the CARRI evaluations were consistent with the intuition of the environmental staff.

Despite assistance from SEMATECH, however, Motorola has thus far been unable to integrate the CARRI software on any network system due to platform incompatibilities. Motorola is now driving towards web-based applications and hopes to convert version 2.0 of the CARRI software to a web platform when it is released by SEMATECH.

#### APPLICATION OF DFE

Using the DFE web-based course and the resources in the environmental group, APRDL is now incorporating consideration of environmental impacts into process development activities. Although the benefits of DFE have not been quantified, it is anticipated that the cost savings in engineering time alone will be significant.

#### Implementation of a New Metallization Technology

It has been anticipated for some time that copper would eventually replace tungsten and aluminum in semiconductor devices. Because APRDL is Motorola's state-of-the-art development lab, it is possible that some development work in copper metallization would take place here at some point in the future. APRDL environmental decided to investigate the potential impacts of bringing copper into a Motorola lab at the earliest possible stage-before copper process development and transfer to manufacturing. A cross-functional team was formed with representatives from APRDL (including APRDL environmental), MRST, manufacturing, and site environmental to identify and investigate potential environmental issues with copper. Using the information from the SEMATECH copper project, the "copper environmental" team was able to identify processes that might involve copper, the environmental issues with these processes and materials, and the potential waste streams from these processes.

The team looked at electroplating and chemical vapor deposition (CVD) as potential methods for copper deposition as well as chemical mechanical polishing (CMP) and test wafer reclaim (copper stripping) as primary sources of copper-containing chemistries. Some of the issues with electroplating were the chemistry of the plating bath, the safety aspects with a new tool design, and the handling of the concentrated plating bath and rinsewaters which would contain copper. Development and manufacturing engineers estimated parameters such as number of tools, probable plating chemistry, bath life, rinse volumes, probable levels of metal for the device, and throughput to determine the volumes of copper concentration of plating bath and rinsewaters. Other parameters that were considered were the site's industrial wastewater (IW) discharge volume and the city discharge concentration limit for copper. Similar parameters were also identified for a wafer reclaim system to strip copper from test wafers. The team concluded that concentrated copper solutions, such as plating and reclaim baths, could not be discharged to the IW drain but would have to be either treated on site or shipped off site. Bath regeneration was also considered, but was determined to not be a likely option in the near term due to lack of knowledge of bath chemistry sensitivities. If electroplating and reclaim systems were installed in the lab with parameters similar to those used by the team for calculation purposes, the rinsewaters could be discharged to the IW drain without further treatment. Based on the suggested plating chemistry from the SEMATECH project, the team determined that there would probably not be any significant worker health issues.

The main issue identified for copper CVD was the reaction chemistry. The team focused on copper(tmvs)(hfac) [(trimethylvinylsilyl)hexafluoroacetylacetonato Copper I) and hfac (hexafluoroacetylacetone) as the copper CVD precursors identified by SEMATECH (and generally known as copper CVD precursors). Because the copper material is not widely used, of primary importance was the TSCA inventory status. If copper CVD was to be used in manufacturing-for either seed layer or full fill deposition-the precursor materials would have to be listed on the TSCA (Toxic Substance Control Act) inventory or have a low volume exemption granted (and the total amount manufactured could not exceed 10,000 lbs per year by all suppliers collectively). The team contacted the primary supplier of these materials and found that the copper material had a low volume exemption granted and that the supplier was working on the premanufacturing notification to the USEPA to have the material TSCA listed. The (hfac)(tmvs) material was TSCA listed. The team also learned from the supplier the general amounts of material required for a specific copper deposition and that 10% utilization was a good approximation for the CVD reaction. The team thus based their calculations on the same device and throughput parameters as the electroplating examples with 90% of the copper material being in the tool effluent, and subsequently being removed in a point-of-use scrubber. This translated to another wastewater stream containing copper that could be discharged to the IW drain. In addition to waste generation concerns, the team met with the site Industrial Hygiene department to address any employee exposure concerns. Although nothing specific was identified, it was determined that some initial area monitoring would be done if a copper CVD tool was brought into the lab.

Copper CMP was another area for potential copper-containing waste. The team chose a specific film thickness of copper to be polished and used the same device and throughput parameter assumptions as with the other copper processes. Assuming all of the copper removed would end up in the CMP slurry and rinse discharge, the team determined that the CMP discharge could probably go to the IW drain and still be well under the city discharge limit. No specific employee exposure issues were identified as the team used a commercially available CMP slurry as the baseline for calculation purposes.

By identifying the environmental impacts of copper processing up front, the team was able to provide management with a strategy for handling copper before copper processing is introduced. These considerations can be used in budget and logistics planning if copper processing becomes a reality. By going through this extensive exercise, the copper environmental team will ensure that no delays are caused by environmental issues.

#### **Introduction of New Materials**

When APRDL first opened its new laboratory in 1995, a baseline of processing materials required for full-flow pilot line manufacturing was identified. Since then, APRDL has evaluated more than 200 new chemicals and gases in various processes. APRDL environmental recognized an important DFE opportunity in new chemical ordering process for review of these materials. APRDL environmental reviews all requests for new materials and also allows the site environmental department to do the same. In this process, the material is identified (MSDS [material safety data sheet] is required) as well as the process in which it will be used, the anticipated usage rate, the procedures for storing and disposing of the material, any expected emissions from the tool, and other pertinent information. By being involved in this process, APRDL and site environmental have been able to identify potential environmental issues prior to the material arriving at the site. TSCA inventory listing status can also be verified prior to the material being transferred to manufacturing. Opportunities to mitigate hazards-or find alternative materials with lesser risk-have frequently been identified. APRDL environmental can now monitor where and how materials with higher environmental risk are being used and can ensure that proper procedures are in place to handle these materials. This procedure was, at first, considered an additional burden for the process engineers requesting materials. Now that the DFE value has been demonstrated, engineers welcome environmental involvement in their chemical and gas evaluations.

#### **Development of CMP Slurry**

APRDL's pilot line CMP area generally uses commercially available CMP slurries for their baseline processes. The development engineers, however, also use the R&D Laboratory to develop their own slurry mixtures for evaluation. This has resulted in the introduction of several new materials to the lab. APRDL environmental works closely with CMP development engineers in this process, particularly since some of the commercially available slurries have some environmental concerns. Consequently, an experimental slurry for a particular polishing application has been developed that is superior in performance to any commercially available slurries, and has significantly lesser environmental impacts. The slurry has a neutral pH, consists of materials with very low environmental risk (CMP engineer claims that you could drink it), and has a reduced abrasive content which may even be eliminated at some point. All components are also listed on the TSCA inventory. The CMP engineers now apply the DFE concept to their daily routine without added burdens and the results have had a significant payback for them.

#### **Evaluation of Wet Cleans Tools**

The APRDL lab has various types of tools in the process areas, including the wet cleans area. When a process is developed and transferred to a manufacturing lab, a tool selection recommendation is often made. APRDL environmental formed a team with cleans engineers, facilities, and site environmental to compare the environmental impacts of two different wet cleans tools. The team also wanted to validate claims by one of the tool suppliers of reduced chemical usage and emissions. The tools are being evaluated based on chemical and DI water usage, emissions, and cost of ownership with an EHS focus (using the SEMAT-ECH tool cost of ownership model [4] with ESH-related costs included). The team is monitoring DI water usage and chemical usage at each tool and is measuring the specific component emissions from the acid and solvent exhausts. This information is correlated with the tool operational logs. After evaluating the data collected and calculating the EHS-related cost of ownership, the team will be able to provide information on the relative EHS performance of the two tools to labs making tool purchase decisions. Other criteria, such as process capability, reliability, and overall cost-of-ownership must also be considered in purchase decisions. The team will also be able to provide the supplier with validated information on chemical usage and emissions.

#### **IPA** Conversion

Motorola had been using methanol as a solvent rinse in one of its manufacturing labs. Methanol, however, is a hazardous air pollutant under the Clean Air Act Amendments. Because the lab's current abatement system for volatile organic compounds (VOCs) cannot destroy methanol effectively, the site could have been subject to the Federal Title V permitting program due to methanol emissions greater than 10 tons per year. After working with the APRDL environmental group, the lab is now converting their processes to isopropyl alcohol (IPA) which is not a hazardous air pollutant and is less toxic than methanol. This conversion will save Motorola up to \$300,000 in permitting costs and will allow Motorola to stay out of the federal permitting program (which would have significantly increased permit modification times and decreased permit flexibility for the site). Furthermore, the site may very well avoid spending \$1-2 million in specific abatement equipment for methanol since the USEPA is considering imposing maximum achievable control standards (MACT) for methanol that could not be attained with the current site abatement. If DFE would have been applied during process development and IPA selected from the start, Motorola would have also saved the cost to requalify the processes.

#### Water Reuse

Motorola labs have several wet cleans tools that utilize water. These tools are often supplied with the proper plumbing to recycle water. However, most labs do not have the network of plumbing to support the water recycle. If this plumbing did exist, it would cost approximately \$7,500 to hold up each wet bench for recycling. Instead, it will cost Motorola \$4.8-\$6 million to retrofit labs. Even at this amount, the payback will only be 15 months.

Water reuse will also have other benefits. Semiconductor facilities are typically the largest consumers of water in a municipality. Some people have estimated that up to 10,000 gallons of DI water may be required to process one 200 mm wafer from beginning to end. Furthermore, the ion exchange process used to produce DI water is the single largest user of bulk chemicals and generates a great deal of waste. This adds significant cost to the products we make. Our industry's water usage is also becoming a major concern for local municipalities and environmental groups. It has the potential of limiting where new factories can be built and may even limit factory production levels. DFE principles will guide Motorola towards water use reduction.

#### **Process Optimization in TEOS Chamber Cleans**

Perfluorinated compounds (PFCs) such as  $CF_4$ ,  $C_2F_6$ , C<sub>3</sub>F<sub>8</sub>, SF<sub>6</sub>, NF<sub>3</sub> and hydrofluorocompounds (HFCs) such as CHF3 are used in semiconductor plasma processes for chamber cleaning and etching. PFCs and HFCs have come under scrutiny recently because they are potent global warming gases with extremely long atmospheric lifetimes. In 1996, the USEPA issued an invitation to members of the semiconductor industry with operations in the U.S. to join a voluntary program entitled "The PFC Emission Reduction Partnership for the Semiconductor Industry." Partner companies agree to endeavor to reduce PFC emissions and to undertake a two year research and development effort to identify means to reduce emissions. Motorola signed a memorandum of understanding with the EPA and became a partner company. Among the many efforts undertaken to reduce PFC emissions, a Motorola lab has implemented some hardware improvements and process optimization methods to reduce C2F6 emissions from a process tool that utilizes a plasma clean. A plenum pumping plate was installed and a one-step cleaning process substituted for the standard two-step process. This has reduced clean time up to 67% and C<sub>2</sub>F<sub>6</sub> usage up to 75%. Throughput has been increased by 10% and Motorola has saved over \$216,000 per year in gas cost. Payback for this upgrade was only 5 months.

#### SUMMARY

Motorola SPS recognizes that early consideration of environmental impacts can result in significant cost savings and cycle time reduction. APRDL, one of the primary research and development labs in the industry, has established an environmental group to work with the process engineers on issues that impact the development lab as well as manufacturing labs that would receive the technology. The web-based DFE course can help engineers understand the concepts of DFE and can provide them with a tool to help them incorporate environmental considerations into their process design and implementation efforts along with other criteria such as cost, performance, and yield. By utilizing these resources, APRDL has been able to begin incorporating the DFE philosophy into the daily routine of the engineers and has been able to demonstrate significant benefits from early consideration of environmental impacts.

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# Cesium-Removal Flow Studies Using Ion Exchange

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The development, selection, and implementation of technologies to be used in removing cesium from radioactive liquid wastes in preparation for their final disposition is discussed.

The methodology involved testing several proposed sorbents in ion-exchange columns using actual liquid wastes from underground storage tanks at U.S. Department of Energy sites. The sorbents initially tested included resorcinolformaldebyde resin (RF), CS-100 resin, SuperLig 644C resin, 3M WEB with embedded SuperLig 644, granular potassium cobalt bexacyanoferrate, and granular crystalline silicotitanates (CSTs).

The results of the bench-scale testing were used to select the sorbent for the full-scale Cesium Removal Demonstration Project (CsRD). This project will treat up to 25,000 gal of radioactive supernatant stored in the Melton Valley Storage Tanks (MVSTs) at Oak Ridge National Laboratory (ORNL). The demonstration system is modular in design and will process supernatant at flows up to 5 gal/min through 12-in.-diam columns. Following the demonstration the system will be used for routine processing of tank waste at ORNL.

To show their applicability to wastes at other sites, RF and CST sorbents were tested in a bench-scale column using a diluted Hanford supernatant liquor (double-shell slurry feed) from tank 241-AW-101. The results are compared with those from tests of MVST supernatant.

#### INTRODUCTION

Cesium and strontium radionuclides are a small fraction of the mainly sodium and potassium salts in underground storage tank supernatants at U.S. Department of Energy (DOE) sites at Hanford, Oak Ridge, Savannah River, and Idaho that DOE must remediate. Cesium-137 is the primary gamma-radiation source in the dissolved tank waste at these sites, and its removal from the supernatant can lower the hazard and waste classification of the treated waste, reducing the costs of further treatment and disposal[1]. Numerous cesium-removal sorbents have been developed by private industry and the DOE Office of Science and Technology. Several of these removal technologies have been previously tested in small batch and column tests using simulated and a few actual supernatants as part of DOE's Environmental Management (EM) programs, including the Tank Focus Area (TFA) and the Efficient Separations and Processing (ESP) Crosscutting Program.

The most promising technologies have now been tested using actual supernatant in both Oak Ridge National Laboratory (ORNL) and Hanford hot cells using flow systems of a scale suitable to obtain engineering data, which have been applied to the design of pilot-scale equipment. The ORNL hot cell tests provided direct input to the Cesium Removal Demonstration Project (CsRD) for sorbent selection. The engineered form of crystalline silicotitanate (C ST) was recommended for the project based on the greatest number of column volumes (CV) at 50% breakthrough, the best test-to-test consistency, and the fewest operational difficulties using the Melton Valley Storage Tank (MVST) W-27 supernatant. The CsRD at ORNL is now treating up to 94,000 L of MVST supernatant from tank W-29 (which was recently transferred from W-27) by using the CSTs. As part of the support to the CsRD, the ORNL hot cell facilities also helped researchers select the supernatant for the CsRD, made it possible to perform the qualification tests for the supernatant and sorbent, generated <sup>137</sup>Cs-loaded CST sorbent for waste acceptance criteria testing using the Toxicity Characteristic Leaching Procedure (TCLP) and for waste-form development testing, and provided operational experience.

#### EXPERIMENTAL SYSTEMS AND APPARATUS

#### ORNL

The equipment diagram for the ORNL hot cell continuous-flow system (Figure 1) consists of the tanks, pumps, tubing and fittings, filters, and instrumentation for testing cesium removal. The system has provided a test bed for investigating new technologies, such as 3M's, and complements other DOE-EM supernatant tasks by using larger engineering-scale continuous equip-

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FIGURE 1. Flow diagram for ORNL cesium-removal system. LLLW = liquid low-level waste.

ment to verify and expand previous batch studies. The operation of both small (1 - to 1 .5-cm-ID) continuous-flow columns and demonstration-scale (30.5-cm-ID) columns will also be evaluated, compared, and contrasted. The ESP and TFA will use the information from these studies to transfer the technologies being developed to the end user.

The tests reported here give direct comparisons of cesium-removal operations conducted in the experimental systems. At ORNL a large (60-L) batch of MVST supernatant from Tank W-27 was obtained in April 1995 to allow the supplied sorbents to be evaluated using the same feed that was initially proposed for the CsRD. Several sorbents were then reevaluated at altered feed conditions and different flow rates, as appropriate, to determine the sorption kinetics. The sorbents were tested at a scale that passed from 0. 1 to 12 L of supernatant continuously through the column at a prescribed flow rate until the <sup>137</sup>Cs concentration in the column effluent reached the desired end point. The progress was followed by using an in-line gamma detector and with samples from a fraction collector. Depending on the sorbent being tested, this required from 15 to more than 1200 CV of supernatant to pass through the columns.

The equipment for the ORNL cesium-removal project in hot cell C of Building 4501, the procedures used during the project, and results of earlier experiments were described previously [2]. Installation of the equipment in the hot cell, development of the procedures and several sorbent tests were completed in FY 1995 and 1996. During tests, the system is operated continuously with in-line monitoring of the column effluent to detect <sup>137</sup>Cs breakthroughs from the sorbent in the module. The monitor is a sodium iodide detector in a lead-shielded container connected to a power supply, amplifier, and Nuclear Data multichannel analyzer system outside the cell. The column effluent passes by the detector head inside a 6.4-mm-OD by 4.8-mm-ID polyethylene tube that has 5 cm of tubing exposed to the detector head. The effluent passes through enough tubing, including the filter system, to ensure that at least 30 min has elapsed between the time liquid leaves the column and enters the gamma detector. This allows any 137mBa, the gamma-emitting decay product of 137Cs, that is present in the feed or in the column to decay (30 min is over ten half-lives for the 2.5-min half-life 137mBa). Consequently, only the cesium that passes through the column is detected by the gamma detector. The configuration of this instrument allows detection of 137Cs levels of 5 to 10 counts/s above background. The 137Cs level in the feed for the detector is about 7000 - 12,000 count/s; thus, the detection limit is about 0.05 - 0.15% of the feed. The counts for the area of the peak for 137Cs were monitored, and the total counts for the selected counting times were recorded by the multichannel analyzer program for later printout.

Once loaded, the column was removed from the experimental system and taken from the cell to measure the quantity of <sup>137</sup>Cs loaded. The columns were counted using an Aptec intrinsic germanium detector with a Nuclear Data multichannel analyzer system. This system allows the columns to be placed at distances up to several meters from the detector head for counting, a requirement necessary for materials that load a high level of radioactive cesium. The column product stream is collected in the fraction collector, and samples of these fractions are counted using a LKB Wallac 1282 Compugamma Universal Gamma Counter. The detection limit for this counter is also about 0. 1% of the feed concentration. Some sorbent eluent samples contained too much <sup>137</sup>Cs for this detector, therefore, they were counted on the Aptec system at 30 cm from the detector head. Some of the fractions that contained solids, or were suspected to contain solids, were sampled through 0.2-µm syringe filters.

The W-27 supernatant used has many similarities to supernatants in tanks at other DOE sites and provided a common basis to test different sorbents for their abilities to remove cesium from actual radioactive storage tank supernatant. In the ORNL system, the sorbents were tested using one 1.5- by 15-cm column containing about 10-12 cm<sup>3</sup> of sorbent at flow rates of 3-9 CV per hour. Other sorbent-containing apparatus such as the 3M WEB were also easily connected to the system. Sorbents that could be eluted and

	TABLE 1. Analyses of the MVST W-27 and W-29 Supernatants				
		MVST W-27 pH 13.3	MVST W-27 pH 14.02	MVST W-29 pH 12.68	
	Radiochemicals	(Bq/mL)	(Bq/mL)	(Bq/mL)	ġ.
	<sup>60</sup> Co	680	330	500	
	<sup>7</sup> Cs	320,000	340,000	460,000	
	<sup>4</sup> Cs	1.400	920	7.600	
	9Sr	65.000	31,000	4,100	
	99Tc	270	51,000	3/7	
	Gross Alpha	0.9	0.4	30	
	Gross Beta	525,000	430,000	550,000	
	Cations	(mg/L)	(mg/L)	(mg/L)	
	Al	0.847	<0.14	4.17	
	As	0.0089	<0.0250	<2.5e-1	
	Ba	8.04	5.61	0.865	
	Ca	89.1	3.1	1.42	
	Cr	2.96	3 49	3 44	
	Cs	0.935	9.95	0.58	
	Cu	<0.0319	0.15	0.07	
	Hg	0.09	0.117	0.258	
	K	10,300	12,000	14,700	
	Ni	1.22	0.73	1.04	
	РЬ	0.0092	<10	2.89	
	RЬ	1.1	2.06	1.28	
	Si		29.3	44.1	
	Sr	.1.0	26.3	1.65	
	Zn	0.473	<0.1485	1.35	
	Anions	(mg/L)	(mg/L)	(mg/L)	- 11
	Br	288	<50.0		
	CI	3,180	2,960	3,050	
	NO <sub>2</sub>		2,720	20,400	
	NO <sub>3</sub>	322,000	298,000	250,000	
	SO <sub>4</sub>	1,540	1,380	15,506	
Anion		(M)	(M)	(M)	and the second
Total ano	in .				
concen Total cati	tration	5.390	6.006	4.475	
concen	tration	5.198	5.832	4.526	
(Differen	ce)	(0.1914)	(-0.1743)	(-0.0503)	
Other <sup>a</sup>				and the second	
TIC me	Л.		300	980	
TOC. m	g/L		390	500	
Density,	mg/L	1.27	1.3	1.233	
TDS, mg	;/L		79,000	81,000	
1 S,mg/L			580,000	390,000	

<sup>a</sup>TC = Total inorganic carbon; TOC = total organic carbon; TDS = total dissolved solids; TS = total solids; TSS = total suspended solids

regenerated were cycled in place through loading, elution, and regeneration. Sorbents were also analyzed by removing the columns from the cell and counting them on a gamma spectrometer to determine the total loading and/or the efficiency of elution.

The MVST W-27 supernatant used for the cesium-absorber tests was originally at pH 7.4; however it was adjusted to match the pH levels in other tanks (pH-12.5-13.3) by adding sodium hydroxide pellets. The supernatant was then settled and filtered. Analyses showed that the original supernatant contained about 3.2 x105 Bq 137Cs/mL, 7.1 x 10-6 M total cesium, 0.26M potassium, 4.7M sodium, and 5.2 M nitrate. For tests to simulate some conditions at other DOE sites, the pH was increased to 14 with sodium hydroxide pellets; cold cesium nitrate was also added to give a total cesium level seven to ten times the original concentration. After these adjustments, the supernatant contained approximately 3.4 x 105 Bq 137Cs/mL, 1.0 x 10-5 M total cesium, 0.31 M potassium and 5.52M sodium; with added cesium, it contained 7.5 x 10-5M total cesium. The concentration of 137Cs in MVST supernatants is one to two orders of magnitude lower than that in some Hanford tank supernatants. The cesium level after the addition of cold cesium approximates the values for Hanford tanks 101-SY and 103-SY (7 x 10-5M) and also that for the double-shell slurry feed (DSSF) simulant. The highcesium feed has a sodium-to-cesium molar ratio of about 74,000 and a sodium-to-potassium ratio of 18.

The supernatant chosen for the CsRD was prepared by adding 50% caustic solution to tank W-27, allowing it to settle for 2 weeks, and then pumping approximately 83,000 L to tank W-29 to mix with the supernatant heel still present after previous operations with W-29. The mixed W-29 was allowed to settle for 1 month and then sampled for the CsRD qualification tests. The W-29 supernatant contained 4.15*M* sodium, 0.38*M* potassium, 4.6 x 10<sup>5</sup> Bq <sup>137</sup>Cs/mL, 4.3 x10<sup>-6</sup> *M* total cesium, 4.0*M* nitrate, and 0.44*M* nitrite; the pHwas 12.68. Approximately 500 gal of W-29 supernatant was then pumped to the CsRD for the first test, which started on September 15, 1996. Measured compositions of all three supernatants used in the column tests in the ORNL hot cell are given in Table 1.

#### Hanford

The Hanford Site's Tank Waste Remediation System (TWRS) organization requested that column-flow tests be performed using selected sorbents with actual Hanford tank supernatant to verify the applicability of simulant data. Such tests may also identify as-of-yet unknown problems or interfer-



FIGURE 2. Diagram of Hanford bench-scale cesium-exchange flow and instruments

ences when processing actual wastes under operating conditions [3]. The Hanford hot cell test apparatus, shown in Figure 2, was described in the test report [4]. The apparatus consists of two sets of test and guard columns, valves, tubing, and a peristaltic pump, all attached to a base and backplate. The columns are 1-cm-ID by 15-cm-tall glass cylinders with bed retainer, 20- $\mu$ m upstream filter, and 10- $\mu$ m bed support. Instrumentation includes an inline gamma-radiation detector to follow the progress of the experiment.

The Hanford test system was designed and built, and the disposable hot cell test apparatus was installed in a hot cell after cold testing and calibration. Both lead columns in each train were filled to a bed height of 10 cm, giving a column volume of about 7.85 cm<sup>3</sup>. The guard columns were filled to about 10 and 7 cm on the A and B sides, respectively. A single pump was used to feed the columns sequentially. The test column was sampled, and the column effluent passed successively through the in-line detector and the guard column. The in-line gamma detector, which is made of cadmium zinc telluride, was placed 60 min downstream of the lead column. The effluent passed the detector within 4.8-mm-ID Tygon tubing.

Approximately 4.5 L of DSSF supernatant liquor from Hanford Tank 241-AW-101 was received through the sampling efforts of the TWRS Characterization Project at Hanford. One batch of the tank waste was diluted with water to the target concentration of 5*M* sodium and processed through the "A" side of the test assembly, through resorcinol-formaldehyde (RF) resin in the primary and guard columns. Eight batches of the tank waste were similarly diluted with water and processed through the "B" side of the test assembly, contacting the CST in both the primary and the guard columns. Analyses of the diluted Hanford feed are shown in Table 2.

The sorbents were tested during treatment of diluted DSSF supernatant to greater than 50% <sup>137</sup>Cs breakthrough. The breakthrough was followed by in-line gamma spectroscopy which allowed adjustment of the sampling routine when breakthrough occurred sooner than originally expected.

Samples of the feeds and column effluents were removed from the cell and submitted for analysis. When the experiment was complete, the RF resin was contacted by 9 CV of 0.5 M nitric acid followed by 5 CV of distilled water. The resin was then removed from the column and digested with 3 Mnitric acid for disposal. The CST sorbent was dissolved in hydrofluoric and hydrochloric acids and diluted with water to allow for further analytical testing and disposal.

#### SORBENTS TESTED

These studies tested the most promising cesium sorbents - those recommended by the ESP and TFA on the basis of previous batch tests at Hanford [5,6], Sandia [7,8], Los Alamos [9], Savannah River [10], and Oak Ridge [11, 12]. SuperLig 644C, batch 3695-GM1121, is a polymer resin of the covalently bound SuperLig macrocycle family of sequestering ligands from IBC Advanced Technologies (American Fork, Utah) and was supplied by Lane Bray, of the Pacific Northwest National Laboratory (PNNL). The RF resin developed at the Westinghouse Savannah River Company (WSRC) was made in several batches by Boulder Scientific (Mead, Colorado). One batch was supplied directly by Jane Bibler, of WSRC (Bibler batch). A second batch was transferred from Bibler to the Radiochemical Engineering Development Center (REDC) at ORNL (REDC batch) [13].

A third batch of RF resin was furnished by AEA Technology from batch BSC- 187 supplied by Bibler (AEA batch). The engineered forms of the CST developed by Sandia National Laboratories and Texas A&M University were produced and supplied by UOP as IONSIV IE-911 lot nos. 07398-38B and 999096810001. The 3M SLIG 644 WWL WEB with SuperLig 644 embedded was supplied by the 3M New Products Department. The granu-

	Feed for RF Columns	Average Feed for CST Columns	
Radiochemicals	(Bq/mL)	(Bq/mL)	
60 <sub>Co</sub>	<225	<233	
137 <sub>Cs</sub>	8,550,000	7.918.000	
154E.	-1 509	-1 602	
1555	<1,370	<1,002	
241 A	<8,4/3	<0,280	
 Am	<19,330	<13,/04	
Cations	(mg/L)	(mg/L)	
Al	15,300	15,500	
As	<40.1	<40.01	
Ag	9.09	8.95	
Ba	<20	<20	
Ca	<40.1	<40.01	
Cd	<2.0	<2.0	
Cr	56.9	59.2	
Cu	<40.1	<40.1	
K	19,800	19,350	
Li	4.36	4.46	
Mo	31.8	31.5	
Na	126,000	126,800	
Ni	<8.02	<8.02	
P	128	151	
Pb	<40.01	<40.01	
S	223	217	
Si	86.6	114	
Sr	<4.01	<4.01	
U	<200	<200	
Zn	9.52	10.1	
Zr	7.73	7.62	
Aanions <sup>a</sup>	(mg/mL)	(mg/L)	
Br	<267	<267	
F	1,110	635	
a	3,140	3,130	
NO <sub>2</sub>	56,100	58,600	
NO <sub>3</sub>	91,100	94,900	
OH	45,900	45 730	
POA	287	525	
SO4	391	315	
4			
Tatal acian ana ana ana	(M) 5.810	(M)	
Total anion concentration	5.819	5.880	
(Difference)	-0.456	-0.371	
 o. b			
TIC mall	962	1 390	
TOC (	802	1,380	
Orelate and	7,400	207	
Oxalate, mg/L	245	29/	
INa/Cs ratio		66,600	

#### TABLE 2. Analyses of the diluted Hanford Tank 241-AW-101 column feed

<sup>a</sup>For corrected dilution

<sup>b</sup>TIC = total inorganic carbon; TOC = total organic carbon.



FIGURE 3. Comparison of sorbents using MVST W-27 adjusted to pH 13.3. FV = filter volumes.

lar potassium cobalt hexacyanoferrate (KCoFeC), lot no. JW-40-021, was made and supplied by Eichrom. The CST used in the CsRD qualification test was purchased by ORNL from UOP as IONSIV IE-911 lot no. 999096810003 for use in the CsRD operations. It was pretreated by the CsRD personnel in the CsRD cold test loop, following UOP directions, and was delivered in slurry form to the hot cell for the small-scale tests.

At Hanford, the sorbents used included RF resin (REDC batch), which was prepared by treating with 10 CV of 0.5 M HNO<sub>3</sub> rinsing with 10 CV of deionized water, and conditioning with 10 CV of 2.5 M NaOH. The CST was provided by UOP, from the Chickasaw, Alabama, molecular sieve plant as IONSIV IE-911, lot no. 999096810001, the same batch used in some of the ORNL studies. It was prepared, in batch mode, by wetting the sorbent and removing the fines. A pretreatment step to adjust the pH of the sorbent to be in equilibrium with the waste solution was completed in batch mode with sodium hydroxide, and the CST was then slurried into the test columns and allowed to settle.

#### **EXPERIMENTAL RESULTS**

#### ORNL

The results for the sorbent materials tested in the ORNL hot cell flow system are summarized in Figures 3 and 4. A sample of 3M SLIG 644 WWL WEB material was contained in a Gelman 25-mm in-line stainless steel filter holder with a filter volume of 1.29 mL. The apparatus was loaded at 1 mL/min (49.78 filter volumes per hour) in an upflow mode through one cycle of loading, elution, and regeneration. Brown color exited the WEB fil-



FIGURE 4. Comparison of cesium sorbents using MVST W-27 adjusted to pH 14.



FIGURE 5. Comparison of the loadings of the CST (-38B, -0001, and -0003) materials using W-27 and W-29 supernatants.

ter for several filter volumes after the supernatant feed began. Loading was 65 filter volumes to 50% breakthrough. The filter was eluted with 0.5 N HNO<sub>3</sub> and regenerated with caustic solution.

Eichrom KCoFeC granular sorbent (7.272 g) was loaded at 9 CV/h using W-27 supernatant at pH 13.32. Normally, KCoFeC is stable at pHs below 12 - 12.5 and is not used above that pH; however, it was tested for completeness. Normal column operation with low cesium breakthrough continued for over 250 CV. The sorbent then began to disintegrate, and the cesium level in the effluent rose rapidly and could not be lowered using 0.2-µm filters.

SuperLig 644C was run at 6 CV/h with 3.779 g of dry resin (11.2-mL volume) using W-27 supernatant at pH 13.3. A considerable amount of color left with the initial few CV of feed through the column. After the breakthrough had reached 50% at about 100 CV, the loaded cesium was eluted with 0.5 N HNO<sub>3</sub> at CV/h. Colored liquid also accompanied the first few CV of acid. The elution curve was very sharp and 95% complete in 6 CV. The resin has a very low density and could be compressed easily (30% or greater). Consequently, calculations were adjusted for the smaller column volume resulting from compression, giving a revised 50% breakthrough of about 138 CV.



FIGURE 6. Overall Hanford RF test results using in-line gamma detector. DI = deionized.

SuperLig 644C was also tested with W-27 supernatant at pH 14.0, using a special device developed by J. L. Collins to keep the bed compact during the volume changes from loading, elution, and regeneration. Loading was done at 3.5 CV/h; the elution used 0.5 N HNO<sub>3</sub> while the bed was regenerated with 2 N NaOH. The first cycle had a total cesium concentration of 1.1 x 10<sup>-5</sup> M in the feed; the following three cycles had 7.5 x 10<sup>-5</sup> M. The bed volume changed by up to 40-50% when switching from feed to deionized water to acid and then caustic and feed. The first loading had 50% breakthrough at about 167 CV. Elution was complete in about 6 CV of 0.5 N HNO<sub>3</sub>. The next three loadings (high cesium) had 50% breakthrough at 50 CV, respectively; initial break-through of the cesium was at less than 10 CV in each case. Two of the loading curves were approximately parallel to the first curve, while the fourth was completely different. Color was seen at the start of each loading and at each regeneration.

RF resin (Bibler batch) was prepared and used in three tests with W-27 supernatant at pH 13.3. At 7 CV/h, 50% breakthrough of cesium occurred at 45 CV. At 2.9 CV/h, it occurred at 36 CV and the shape of the curve was similar to, but steeper than, that in the 7-CV/h RF run. In the third test, RF resin was loaded, eluted, regenerated, and then rinsed five times at 6.0 CV/h. During each cycle, brown-colored liquid exited the bed for the first 3-4 CV of feed or regenerant. The 50% breakthroughs were consistent at about 45 to 50 CV, but some operational problems began to develop during the last two loadings. Elution was completed with 0.5 M HNO<sub>3</sub> at about 3 CV/h, and the resin volume shrank from about 10 to about 5.5 cm<sup>3</sup> during each elution. Approximately 9-12 CV was required for cesium elution to be essentially complete (>95% cesium removal from the resin).

RF resin (REDC batch) was also loaded with W-27 supernatant feed at pH 14.0 that contained 1 x  $10^{-5}$  M cesium at 3.5 CV/h to 70% break-through. The Collins device previously described was also used during this test. Cesium initially broke through at 7 CV, and the curve was then very steep to 50% at about 18 CV. The elution was accomplished with 0.5 N HNO<sub>3</sub>. A sample of this batch of RF was transferred to Hanford for use in their test with the DSSF feed and had a 50% breakthrough at 14 CV.

A third RF resin (AEA batch) was loaded with W-27 superuatant at pH 13.3 at a feed rate of 6 CV/h. The loading was continued through 75 CV,



FIGURE 7. Hanford RF cesium-removal results, in-line vs. wet gamma energy analysis. All in-line values corrected for background.

with the breakthrough reaching only about 1.1-1.2%. The loading curve shows that the initial breakthrough did not occur until 15 CV, and the curve was then very shallow to 1% at about 65 CV. Brown color was also seen in the effluent.

CST from UOP, IONSIV IE-911 lot no. 07398-38B, was first tested at 3 CV/h in downflow mode using W-27 supernatant at pH 13.3 for a total of over 435 CV. No problems that could be attributed to the ion exchanger occurred during the continuous run of more than 6 days (24 h/day). The 1% breakthrough came after 100 CV, 10% breakthrough at about 190 CV, and 50% breakthrough at 350 CV. At 6-CV/h loading, the 50% breakthrough of cesium was very close to that obtained at 3 CV/h (i.e., 340 CV). No difficulties were observed with the system during either loading.

A third sample of the CST-38B (11.873 g and 10.4-cm<sup>3</sup> column volume) was loaded at 6 CV/h with W-27 supernatant at pH 14.0 and a cesium concentration of 7.48 x 10<sup>-5</sup> M to greater than 55% breakthrough. The loading curve was parallel to the previous 6 CV/h curve, as expected, with the 50% breakthrough occurring at 272 CV (about 79% of the breakthrough for feed with lower cesium and hydroxide), the 10% breakthrough at 122 CV, and the 1% breakthrough at 55 CV. Again, no difficulties were observed during operation.

A column that contained 10.59 g (10.35 cm3) of UOP IONSIV IE-911 (lot no. 999096810001) CST, the production-engineered form of CST from the Alabama UOP plant, was used in a repeat of the previous run using the pH 14 high-cesium (7.5 x 10-5 M) feed at 6 CV/h. However, a lower-cesium-concentration feed (1 x 10-5 M) was used in the last 150 CV. The sorbent was treated to remove fines (2-3%) because the CST was fairly dusty and the water was milky after first contact. Initial flow-stabilization problems caused an erratic startup. Once flow had been stabilized, the breakthrough curve returned to the level of background before starting the normal increase. The 50% breakthrough was at 294 CV, the 10% breakthrough at 127 CV, and the 1% breakthrough at about 61 CV. This was about 3 - 10% better than the -38B material at the above breakthrough points. Because this CST is about 10% less dense than the -38B, the performance per mass of sorbent is roughly 10 - 20% better. No difficulties with the system were observed during operation; however, it was noted that the pH of the supernatant was reduced by the CST as it passed through the column for the first 100 CV. This is important to note if the supernatant contains any soluble aluminum that could precipitate in and on the bed if the pH drops even slightly.



FIGURE 8. Hanford CST test in-line gamma detection vs. wet chemistry. All in-line values corrected for background.

For the CsRD qualification of CST IONSIV IE-911 (lot no. 99909681003) and W-29 supernatant, the CST was pretreated to pH 12.6 with caustic and then fluidized to remove fines using a simulant containing 4.5 M NaNO3 and 0.1 N NaOH. The W-29 supernatant was sampled from the tank in three 7-L bottles and transferred to the test building. The supernatant in one bottle was then placed in the cell and passed through a 25-µm filter prior to entering the column. A column with 10.4 cm3 of the treated CST was loaded at 6 CV/h (8.426 gal · h-1 · ft-2) for 560 CV with a minor upset at about 50 CV, but the test was completed uneventfully during the next 500 CV. Data for the cesium analyses give 50% breakthroughs of 503.7 to 546.2 CV for 137Cs analyses, depending on the analytical method. The analyses showed that the CST loaded Ba, Ca, Cs, gross alpha and beta, 90Sr, U, and Zn; however, Hg, Cd, 99Tc, Cr, 106Ru, Rb, Ni, Na, K, and Al were not loaded. A comparison of the CST runs with W-27 and W-29 supernatants is shown in Figure 5. The 45% increase in the CV processed to 50% breakthrough (from 345 for W-27 to 505 for W-29) can be attributed to the lower total cesium and nitrate concentrations of the W-29 supernatant. The plot also shows the previous curves for comparison and indicates that the performance of CST decreases with increasing nitrate and increases with increasing pH. The apparent breakthroughs for uranium, 90Sr, and lead were 433, 1164, and 3327 CV, respectively. Sorbent from the loaded column was subjected to a modified TCLP procedure, which showed no unacceptable values in the leach solution.

#### Hanford

The feed preparation for the Hanford RF test resulted in a batch of supernatant with no evidence of solids. The supernatant was fed through the columns at a rate of 4.14 CV/h (10.16 gal  $\cdot$  h<sup>-1</sup> · fr<sup>-2</sup>) for 25 CV. The 50% breakthrough occurred at about 14 CV, which is early compared to what would be expected based on the earlier batch testing. Normalized to a 5 *M* sodium basis, it occurred at 15.8 CV. The loading curve for the run is shown in Figure 6. Analyses of samples of the feed solution, effluent, eluate, and spent resin digest provide no conclusive evidence of any retention of the P, S, Cr, Mo, Zn, and Si on the resin. The trace gamma data for <sup>134</sup>Cs provide good correlation with the <sup>137</sup>Cs data, remaining in linear proportion throughout the test. Trace quantities of alpha-emitting isotopes were present in the feed, but they were not found at greater than 10% of the feed concentration in the effluents.

Comparison of the in-line gamma-counter analysis for <sup>137</sup>Cs with the wet-radiochemical analysis of fraction samples yielded excellent agreement for both the shape of the curve and the 50% breakthrough,

TABLE 3. Comparison of sorbent results for ORNL Cell C continuous-column cesium-removal experiments

	MVST W-27	Flow Rates	Loading	CV	to breakthro	ugh	Comments
Sorbent	feed supernatant	(CV/h)	Cycles	1%	10%	50%	
Cs-100	pH 13.2; Cs= 7.5E - 6M	3	1	3	7	18	No longer commercial
RF (Bibler - 1995)	pH 13.3; Cs =7.5E - 6M	3	1	12	20	35	Color; skrink-swell
RF (Bibler - 1995)	pH 13.3; Cs = 7.5E - 6M 7.5E-6M	6	5	4	11	40	Color; operational
RF (Bibler - 1995)	pH 13.3; Cs= 7.5E-6-M	7	1	7.5	17	48	Color
RF (REDC-Bibler)	pH 14.02;Cs = 1E-5M	6	1	10	14	18	Color
RF (AEA-BSC-187)	W-27; pH 13.3	6	1	65	140		Color; poor elution
SuperLig 644C	W-27; pH 13.3	3	1	20	65		Color; low density; swell/shrink
SuperLig 644C	W-27;pH 13.3	6	1	1	10	100	Color; lowdensity; swell/shrink
SuperLig 644C	pH 14.02; Cs = 1E-5	3.5	4	15	46	166	Color; good elution; volume changes;
	(cycle1); 7.5E - 5M			4.5	16	70	poor reproducibility
	(cycles 2-4)			15	31	70	
				2	6	50	
3M SLC WEB	W-27; PH 13.3	49.8	ī	18	38	60	Color: swell: poor elution
KCoFeC	W-27; pH 13.3	9	1	85	250	250	Disintegrates at pH; fines
CST-38B	W-27; PH 13.3	3	1	114	192	350	No problems
CST-38B	W-27; pH 13.3	6	1	82	174	342	No problems
CST-38B	pH 14.02; Cs = 7.5E - 5M	6	1	55	123	273	No problems
CST-0001	pH 14.02; Cs = 7.5E - 5M	6	1	60	129	296	No problems
CST-0003	W-29; pH 12.6	6	1	100	226	505	No problems
	Cs= 4.4E - 6M						(in non-1) 1000

each yielding 14 CV as shown in Figure 7. Many of the metals (Ca, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Si, and Zn) that were below the detection limit in the feed and effluent samples were detectable in the eluate from 0.5 M nitric acid elution. The 9 CV of acid elution provided essentially complete removal of the cesium that had been retained on the lead column.

Following completion of the RF test, the feed for the CST test was prepared and started at a desired flow rate of 6 CV/h, with sampling at about 25-CV increments and a total flow of 840 CV. After completion of the feeding, the lines and columns were flushed with caustic solution. This resulted in unanticipated plugging of the beds, presumably due to precipitation of aluminum compounds and blinding of the bed filters when the hydroxide concentration was lowered. After the sorbent had been digested with hydrofluoric and hydrochloric acids, samples of the feed batches, primary column effluents, guard column effluents, feed solids, and column digests were removed from the cell and analyzed.

Results of the CST experiment indicated that the 50% breakthrough occurred at 696.8 CV, at a feed rate of 6.27 CV/h (15.38 gal  $\cdot$  h<sup>-1</sup> ft.<sup>2</sup>). Analytical results for the effluent samples showed that most metals did not load on the CST. A comparison of the in-line gamma detection and wet-chemistry gamma analysis is shown in Figure 8. As shown, the two methods gave identical responses. Further analyses of the guard-column composite samples for the anions and cations showed that  $^{60}$ Co,  $^{238,239}$ Pu , and  $^{99}$ Tc were detectable primarily because of the large sample volume and the decontamination of the sample by the two CST columns.

Following test completion, the system was flushed and the ion-exchanger columns were removed from the assembly. The sorbent was removed from the columns and dissolved in hydrofluoric and hydrochloric acids; aliquots were diluted with water and removed from the cell for analysis.

#### DISCUSSION.

Recently, cesium-sorbent studies in actual and simulated alkaline waste matrices were completed using powdered and developmental engineered CST materials at the PNNL [14. 15], ORNL [11.12], and Sandia National Laboratories. In addition, a large body of cesium ionexchange data has been collected for the RF resin in simulated and actual waste matrices [6, 11, 12, 16-18]. Furthermore, the chemical and radiation stabilities of several organic ion-exchange resins have been investigated by numerous researchers [16-19].

A small-scale laboratory batch experiment evaluating several ionexchange materials for the removal of cesium from simulated and actual Hanford alkaline supernatant has been described [15]. The following were compared as a function of solution composition, supernatant-to-exchanger phase ratio, and multiple sequential contacts: cesium batch distribution ratios ( $K_d = (C_i - C_f)/C_f * V/M$  where  $C_i$  is the initial ion concentration in the feed solution,  $C_f$  is the final concentration, V is the solution volume in milliliters, and M is the exchanger mass in grams); column distribution ratios ( $\lambda = K_d \times \rho_b$ , where  $\rho_h$  is the sorbent dry bulk density); and decontamination factors. Equilibrium results for the RF showed a range of  $\lambda$  values from 100 to 2,000, depending on the sodium concentration, at the same sodium:cesium ratio. Over the same range, the  $\lambda$  values for CST-38 B ranged from 1000 to >20,000. When the exchanger results were compared with those using actual waste, the greatest deviation in performance was noted for the RF resin, which had about 25 to 50% lower values across the range, and for the CST-38B at the highest sodium:cesium ratios, which had a 35% drop in performance. (All exchangers, however, showed decreased performance.) Most of the ORNL RF column experiments resulted in 50% breakthroughs at CV values 2-5 times lower than expected - probably due to resin degradation during storage. Comparable experiments using the RF resin supplied by AEA showed 50% breakthrough predictions of greater than 100 CV with the same W-27 used earlier; this result adds credence to degradation being the cause of the poor performance.

In the tests with actual DSSF waste, the sample of waste used was a composite from tanks 1101-AW (70%), 106-AP (20%), and 102-AP (10%) diluted to 4.96  $\pm$  0.19 *M* sodium and 0.478  $\pm$  0.012 *M* potassium with an initial Na:Cs ratio of 78,000. Under these conditions, the batch distribution ratios obtained with the CST and RF materials predicted approximately 700 and 65 CV, respectively. These data compare favorably with the current column test results of 696 CV for the CST



FIGURE 9. Flow diagrams for the ORNL CsRD: (a) process flow for the CSRD and (b) resin loading and unloading.

IE-911 but not for the RF resin. Differences between the current RF experiments and the previous batch tests are probably related to the chemical instability of the resin during storage since very similar results were obtained with the same resin in the two separate tests at ORNL and PNNL [17-19].

Poor performance can also be caused by the effects of the resin or particle density during column testing, which may not be seen during small batch tests. If the resin is very light, it can almost float and result in an unpacked column, which resembles a fluidized bed in its removal capabilities. This can cause very early breakthrough of the cesium due to the dispersion through the bed. Indications of density and bed-height effects were seen with RF resin in several experiments and modeling efforts (described by Linda Wang of Purdue University in 1996). It was shown that in the case of RF resin, a ratio of 15 for bed length to diameter was required before fixed-bed behavior with a constant pattern was observed. The Hanford RF column had a height-todiameter ratio of 10; the ORNL column had a ratio of 4. As a result, a weighted-bed follower, described earlier, was successfully used for the ORNL RF and SuperLig 644C loading and elution at pH 14 conditions. Other possibilities for poor breakthrough curves for the RF resins are improper preconditioning of the bed and mismatching of bed presaturant and column feed, both in salt concentration and in density. Some of these conditions could have had an effect on the runs with W-27 for the organic resins because in some cases they were washed with water before the W-27 feed (5 M salt) began.

Comparison of the ORNL column data for all sorbents used with the W-27 feed with data obtained using simulant and actual supernatants at other sites showed good agreement and predictability from batch equilibrium to column testing except for the RF resin, which varied greatly from batch to batch. Further comparisons must take into account not only cesium concentrations but also the pH, the other anions and cations in the supernatant, and the ratios of other cations to the cesium concentration.

These comparative evaluations helped provide critical data for the selection of the sorbent for the CsRD as well as data applicable to other DOE sites. In addition to the cesium-removal capacity of the materials tested, the operational characteristics during continuous-loading experiments were monitored. The organic sorbents, RF and SuperLig 644C, and the 3M SLIG 644 WWL WEB material yielded colored products upon the first introduction of feed or during regeneration after elution. They also exhibited volume changes during various stages of the preparation, loading, elution, and regeneration. In some of the experiments, solids were present in the effluent that collected in the equipment downstream from the column or module. The high pH of the feed supernatant to the Eichrom KCoFeC resulted in its chemical breakdown and loss in the column effluent. No operational problems were noted for the CSTs, although preparation of the commercial forms required equilibration with caustic solution and fluidization to remove fines.

As shown with ORNL and Hanford supernatants, the CST materials performed better overall than any of the other materials at all conditions tested. The best kinetic performance occurred at 3 CV/h. The CST was also able to maintain the column effluent at less than 1% breakthrough for much longer than the other materials except the RF (AEA batch). This means that the effluent through the CST columns contained lower levels of cesium (e.g., if C/C<sub>0</sub> is 0.01, then 99% of the cesium is removed from the supernatant) compared with the SuperLig 644C, which showed breakthrough in less than 10 CV. The last RF run with the AEA batch of RF resin, although not taken to 50% breakthrough, showed much improved capacity over the two batches of RF that had been previously tested, and the results were closer to those predicted on the basis of the earlier batch contacts.

Comparison of the column data obtained for the W-27 and W-29 feed with the Hanford data obtained for the DSSF feed with data obtained using simulant and actual supernatants in other tests showed good agreement and predictability from batch equilibrium to column testing. There were exceptions, and the comparisons must take into account the cesium concentration; the hydroxide concentration, the other anions and cations in the supernatant; the ratios of the other cations to the cesium concentration; and, for the RF resin, the degree of degradation during storage.

The results summarized in Table 3 provided critical data for selection of the sorbent for the CsRD. In addition, the operational characteristics during continuous loading experiments were monitored.

#### **CESIUM REMOVAL DEMONSTRATION PROJECT (CSRD)**

The CsRD addresses the fundamental need to selectively remove cesium from the bulk supematant and concentrate it into a small-volume, stable waste form. The CsRD effort supports enhancement to baseline waste-processing efforts at ORNL and Hanford and offers an alternative at Savannah River. The objectives of the project were as follows:

 generate full-scale operating data with demonstrated ESPdeveloped sorbent;

• evaluate the use of mobile, modular equipment for the treatment of high-activity waste;

• evaluate decontamination metods for hands-on maintenance;

• obtain data to show the relationship between bench-scale and full-scale performance;

• provide material to the Savannah River Site for a vitrification demonstration project; and

 provide a unit for baseline low-level radioactive waste operations at ORNL.

With these objectives, a team was selected to begin the design, development, procurement, and construction of the CsRD. The design alternatives study was completed under the direction of ORNL, and TTI Engineering was chosen to build the mobile modular CsRD system. Flow diagrams of the system for both sorbent loading with supernatant and sorbent transfer are shown in Figure 9. The CsRD consists of a 500-gal feed tank and a filter column followed by two ionexchange columns that can be operated separately or in series. The sorbent is slurried into columns before a test is started, and it is then removed as a slurry to a drying drum for final dewatering before shipment.

After the tests previously described, UOP was contracted to provide the CST batch for the initial demonstration using up to 94,000 L of MVST supernatant. Once the CsRD system was delivered, ORNL personnel installed the modular, mobile ion-exchange system in existing facilities to begin the full-scale demonstration based on bench-scale qualification tests performed at ORNL using the same batch of CST and MVST W-29 supernatant previously described. The bench-scale tests also provided loaded CST sorbent for TCLP leach testing to meet waste acceptance criteria at potential disposal sites.

Major accomplishments for the CsRD as of the end of FY 1996 have included placing the contract with TTI Engineering for the CsRD system, completion of the design and design review of the system, construction and installation, cold testing, and completion of all necessary documentation with federal and state agencies. Startup with actual radioactive supernatant was completed on schedule, and the first 2000 L of W-29 supernatant was treated. No column problems were encountered during this initial operation. The end point of this run was to be the loading of approximately 25 Ci of <sup>137</sup>Cs on the bed.

During FY 1997, up to 94,000 L of MVST supernatant will be processed and the effectiveness of cesium removal evaluated. Another goal is to minimize exposure to operating personnel so that the system can be successfrilly used in long-term treatment operations. It is also important that the unit be successfrilly decontaminated to enable hands-on maintenance and transfer to other sites. Some of the cesiumloaded CST is being tested as a final waste form, and some is being made into a glass to evaluate effective management methods for the spent ion-exchange material. It is hoped that the CsRD will make it possible for industry and universities to participate in the development of improved sorbent and help in modeling of the data comparing bench-scale with frill-scale systems. The successful completion of the project will create opportunities for full-scale treatment at DOE sites.

#### SUMMARY

Technologies evaluated in these tasks apply to the remediation of tank waste supernatants at most DOE sites, particularly highly alkaline supernatants that contain high concentrations of salts. Separation and concentration of the soluble radionuclides, particularly cesium, would result in a much smaller amount of radioactive waste for disposal or long-term storage. The CsRD at ORNL is operating with the UOP CST in treating up to 25,000 gal of MVST supernatant and will be transferred to the site operations personnel at the completion of testing. Removal of the radioactive cesium will also reduce shielding requirements and make downstream handling much easier for removing nitrates and/or any other toxic or hazardous components in the salt solution.

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# **Recovery, Reuse, and Recycle of** Water in Semiconductor Wafer **Fabrication Facilities**

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This paper summarizes the benefits and risks associated with water re-use and recycling in the semiconductor industry. The specific items that will be covered in this paper are: characterization of the spent rinsewater types, the composition range of key impurities, different recycling strategies, and water conservation methods. Discussion will include the development of new purification methods for the removal of organic impurities, and the development of a computer model for simulating the effects of recycle.

#### INTRODUCTION

The semiconductor industry has recently experienced rapid growth at an unprecedented rate. This expansion is causing concern in some communities due to the large quantities of water presently required for semiconductor wafer manufacturing. Along with this expansion cones the construction and installation of new wafer fabrication facilities (FABS). Each new facility willuse 1 to 3 million gallons per day. The water use in some locations approaches several milions of gallons per day. The only cost effective long-term solution is the proper segregation and collection of waste rinsewaters and the implementation of a true recycling strategy.

#### **TABLE 1. Benefits Associated With Recycling Water**

- 1. Improved feed water quality, final UPW quality
- 2. Improved reliability of UPW facility, Less downtime: Reduced frequency of RO membrane cleaning processes. Reduced frequency of ion exchange regenerations. Reduced frequency of filter backwashes/rinses. Improved efficiencies in UPW treatment processing,
- 3. Reduced chemical usage for ion exchange regenerations.
- 4. Signified cost savings: Less feed water and wastewater discharge costs. Less regeneration chemical cost. Less industrial waste treatment cost,
- 5. Improved RO reject quality for other reclamation purposes. 6. Less demand on the municipal water supply and waste water treatment systems.

#### TABLE 2. Risks Associated With water Recycling

- 1. The introduction of impurity spikes into the system.
- 2. The buildup of recalcitrant compounds.
- 3. Inadequacy of the present purification methods in removing process generated compounds.
- 4. Risk of new chemical interactions caused by recycle.
- 5. Contamination due to biofouling.

Recycling of water that was previously purified to an ultrapure level and then used to rinse off ultrapure chemicals from clean wafers, provides many advantages, including an improvement in final water quality. This alone

A Sample of 1996 Ultrapure Water Use Among SEMATECH



This chart represents ultrapure water (UPW) used in wafer processing (not local resources) at 16 U.S. chip manufacturing facilities. Total demand on local resources has been reduced by many companies through implementation of recycle reclaim strategies. SOURCE: SEMATECH

FIGURE 1. Ultrapure water use in semiconductor wafer processing.



FIGURE 2. Typical process tool setup.

justifies the efforts associated with the implementation of a recycle strategy. It is not necessary to justify the effort based only on water conservation principles. There are many benefits to be realized, both in cost and in processing, associated with recycling once purified water, back through the purification process again. Much of the spent rinsewater generated in the semiconductor processes, is still of superior quality compared to most municipal feedwater supplies, This spent rinsewater can be used as a feed water source, replacing a portion of the municipal feedwater supply, to be reprocessed in the ultrapure deionized water (UPW) facility. The benefits to this are multi-fold, and include the items listed in Table I.

There are also risks, however, associated with recycling spent process rinsewater back into a UPW facility, to be used once again in the wafer fabrication process. These risks include the items listed in Table 2.

#### DISCUSSION OF WATER CONSERVATION STRATEGIES

Figure 1 shows the wide range of water usage rate reported by semiconductor manufacturing plants. This chart is the result of a survey performed by Sematech and the data obtained from its member companies. The amount of Ultra Pure Water (UPW) used per wafer produced varies from site to site, from company to company, and with wafer size. Each wafer fabrication facility typically uses 1-3 MGPD (million gallons per day). Some company sites have 3-4 fabs per site, resulting in large quantities of UPW use per site which can easily exceed 10 MGPD. This data is not the amount of municipal water demand, but the amount of UPW. The actual demand on municipal water supply is approximately 25% greater than the quantity of UPW, due to losses in the water purification process. The demands can be quite significant on the municipal water supply and have been a problem for some communities, especially those located in arid regions. Most of this UPW is used for wafer rinsing purposes. Figure 2 indicates some typical semiconductor process tool setups and a general indication of the various types of wastewater generated (DeGenova and Williams [2]).

Typically, ultrapure rinse water is contaminated with residual chemicals carried in with the process flow. The ultrapure rinse that typically follows acid/base treatments usually can be readily recycled; the contaminants are removed from the water using standard separation techniques. Hence, these streams are considered easily recyclable. One must only segregate the rinse water drains away from the industrial waste drain to collect the water for recycle purposes. Due to the nature of the semiconductor chemical process steps, however, some of the rinse water becomes contaminated with compounds that are not readily removed with standard separation techniques. Although they follow acid/base chemistries, the actual product itself may carry contaminants into this rinse water. The rinse water, from the resist strip hoods, may

#### **TABLE 3. Rinse Water Reduction**

<ul> <li>Spray rinsing vs. C</li> </ul>	Overflow, Quick	Dump
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- Rinse Tank Geometry Improvements
   Hot UPW vs. Cold UPW
- Megasonic Rinsing
- Idle Flow Rate Reduction
- Analystical Monitoring of Rinse Water
- Computer Modeling; Convective/Diffusive

not be readily recyclable. The rinse that typically follows organic chemical baths may also become contaminated with compounds not readily removable and recyclable. The segregation of these waste streams is important to achieve a reliable recycle system.

The contaminants in the spent rinsewater generating most of the concern in the industry today are organic solvents. The method of



FIGURE 3. Typical overflow rinsing

#### TABLE 4. Water Reclamation/Reuse

- RO Reject; C/T, Air Scrubbers, Irrigation
- Ultrafilter Reject; UPW System Rinsing
  Analytical Instrument Discharge; Various Use
- Spent Rinse Water; C/T Makeup

opene rense water, or 1 maneup

choice for the removal of these organic compounds is oxidation. Filtration and adsorption present a risk of biofouling. The concept of photocatalytic oxidation reactors, as applied to recycle systems, has been developed at the University of Arizona in Tucson (Chen and Shadman; Shadman and Governal [1]). The photocatalyzed oxidation of processgenerated impurities like surfactants, organic solvents, and trace chlorinated hydrocarbons in ultrapure water is promising.

Process simulation is another important tool in the design and analysis of recycle systems. Work is presently underway at the University of Arizona (Shadman [5]) in developing a process simulator for this application. This simulation consists of a solution to the governing equations for transport and removal of impurities. The equations for the simulator modules representing reactions and transport of impurities are combined

#### **TABLE 5. Water Recycling**

- Spent Rinse Water: Recycled to UPW System;
- Feed Water Storage Tank
- Semi-Pure Storage Tank
- Ultrapure Water Storage Tank

to determine the processes that take place in a typical ultrapure water treatment facility. In solving these equations, one can obtain the dynamics of contaminant distribution in the primary supply and the polishing loop as well as the final concentrations at the point of use.

The primary strategy to conserve UPW is by reducing the water used for water rinsing. Some of the techniques, indicated in Table 3, are quite simple but can make significant impacts to the overall water consumption. Spray type rinsing has been shown to use much less water than typical overflow type. However, spray rinsing generally adds dissolved oxygen and possibly other contaminants.

Hot water is generally more effective than cold water in cleaning wafers. In some cases, the rinse water temperature can be elevated to

#### **TABLE 6. Typical Water Quality Comparison**

Water Quality Parameter	Units	Typical Municipal Water Supply	Typical Ultrapure Water Pruduct	Segregated (50%) Spent Rinse Water
Resistivity	M Ohma-cm	0.004	>18	0.8
pH	units	8	6	5-7
TOC	ppb	3500	<10	20
Ammonium	ppb	300	<1	300
Calcium	ppb	22000	<1	68
Magnesium	ppb	4000	<1	26
Potassium	ppb	4500	<1	25
Silica	ppb	4780	<10	338
Sodium	ppb	29000	<1	237
Chloride	ppb	15000	<1	100
Fluoride	ppb	740	<1	100
Sulfate	ppb	42000	<1	500

accomplish a better rinse, reducing the quantity of rinse water required. However, hot ultrapure rinse water has also been shown to cause defects after certain process steps. Megasonic rinsing is another method of improving the rinse process. By adding megasonic action, one can improve the rinsing process in some cases, thereby reducing the required quantity of rinse water. Until recently, rinse tanks were typically designed with large volumes . It was originally thought that large water volumes would provide a cleaner rinse. Nonetheless, Figure 3 shows this is not necessarily the case. As the wafers are typically loaded into wafer carriers, or boats, and are tightly spaced relative to one another, the path of least resistance for the water flow is actually around the wafer boat, rather than in between the wafer product spacing. It has been shown that nearly 80% of the rinse water actually bypasses the product (Rosato et al. [4]). A smaller rinse tank actually provides for a better rinse process with this arrangement. New semiconductor process tools are being designed with smaller rinse tanks and with directional flow patterns forcing the water in between the wafer spaces, producing faster, better rinsing. Less process time for rinsing is required and better process control is achieved.

In addition, reducing flow rates during idle periods can also make significant differences in water reduction. However, low flow rates can lead to bacterial growth, which could be devastating to the UPW system and to the production line. Studies are underway to evaluate sensors for



#### FIGURE 4. Water recycling strategies.

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FIGURE 5. Typical UPW system with recycle. Recycle effects on water quality levels.

monitoring the quality of water in each rinse tank to determine when adequate rinsing is achieved. Some studies have focused on the development of rinse models using both diflusion and convection equations to help optimize the rinsing process (Helms [3]). These models include the processes that occur in between the tight wafer spacing, including the desorption of the removal of chemicals from the wafer surface and the diffusion of the chemicals through the boundary layer into the bulk fluid where impurities are carried away by convection.

A second water reduction strategy currently underway is in the reuse of water in other areas such as in the cooling towers, air scrubbers, and non process applications. The reject water from the reverse osmosis process is a good candidate for this type of re-use. Some of the more common applications of water re-use are listed in Table 4. Spent rinse water can also be used for some of these re-use applications. However, due to its relatively pure nature, this water is quite aggressive and will attack most materials. Additional treatment may be necessary prior to re-use of this water, such as in raising the alkalinity to decrease the corrosion characteristics.

Another water use optimization and reduction strategy is in recycling of the spent rinse water back into the UPW treatment system. Because of the relatively high purity level of the rinse water, one can consider recycling this water back into the UPW process at various points within the process. It can be combined with the feed water at the treatment process input, thereby reducing the demand for this feed source. It can also be combined at other points in the UPW system, such as with reverse osmosis purified water, in a semi-pure state. Or, one can consider recycling this spent rinse water back into the UPW process at an ultrapure state, such as in the ultrapure water storage tank where it will be re-polished prior to use. Table 5 lists these options, which are also illustrated in Figure 4, which indicates a typical UPW treatment process, with primary treatment, ion exchange or secondary treatment, and a final polishing treatment step with holding tanks. The spent rinse water can be brought back to any of these holding tanks. Naturally, the highest benefit would be gained by bringing the recycle back to the UPW tank prior to polishing. However, this option also carries the highest risk.

Table 6 indicates some typical water purity levels at different stages of processing. Shown here are a typical municipal supply water purity, a typical Ultrapure Water quality, and what one would expect from collecting approximately 50% of the spent rinse water, specifically segregated according to recycle readiness.

Table 6 indicates that the spent rinse water is still in a semi-pure state, and is of better quality than water supplied by the municipality. It seems quite logical that replacing the municipal city feed water supply with this spent nnse water in a recycle mode would have beneficial consequences. However, due to the risks associated with recycling these spent rinse waters back into the process flow, the consequences of which could be devastating to manufacturing, a much more detailed effort is required. If the final UPW product becomes contaminated at any time, the manufacturing facility must stop production, risking all work in progress. It may take significant time to bring the UPW quality back to the required specifications, thereby causing downtime and extra costs and risks. The task at hand is to eliminate any risk associated with water recycling.

The benefits of recycling, listed in Table I, can be quite substantial. With a better quality of feed water at the source, the unit processes in the ultrapure water facility operate with improved efficiency. Due to the improved processing, there is less required maintenance and downtime, resulting in a more reliable, and safer facility. A reduction of chemical usage can also be realized, as less membrane cleaning and less ion exchange regeneration are required. There is also a reduction in the amount of industrial wastewater requiring treatment. In fact, with a better quality feed source, reject from a reverse osmosis system also improves in quality, rendering this water much more amenable for other reclamation purposes. Figure 5 illustrates a schematic of a typical UPW system with recycle back to the primary feed water storage tank. Indicated here, are quality levels through various points in the UPW facility, with and without the recycle of water. The estimated water quality with recycle, based on quality levels listed in Table 6, feeding the final polishing loop is of superior quality.

The risks, listed in Table 2, include bringing new and unknown process contaminants to the UPW system. Compounds not properly removed could build up in the system. The product yield could then be negatively impacted. There is very little data available on the removal of organic compounds typically used in wafer processing. Any of these compounds in the UPW product at the point of use could be devastating. Hence, the proper segregation of the spent rinse water is imperative in order to keep these compounds out of the recycle loop, at least until data is available for the removal of these compounds with existing technology, and/or until newer and more effective technologies can be developed.

In addition to the process simulation, improved metrology and sensing techniques are required to minimize the recycling risk. Of utmost importance is on-line instrumentation with fast response that can be used to monitor recycle water quality. The fast response is necessary so that quick decisions can be made on whether to direct the recycle water back into the UPW process, or to divert the flow away from the UPW process. This action must be fast enough to avoid any quality upsets. Special valve switching arrangements can be installed, based on the monitoring devices, in order to minimize the risk or system upsets. Eventually, there will be a need to integrate the metrology and the simulator for both predictive and control purposes.

#### SUMARY AND CONCLUSION

A water recycling strategy focused on the segregation and re-use of semi-pure rinsewaters will provide for a cost effective system. Many benefits can be also be realized in the area of final UPW product quality, safety, waste chemical reduction, energy reduction, and improved process reliability.

There is a definite need for process simulation and more advanced metrology and control techniques. The risks associated with recycling can be minimized and managed properly.

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## Modeling and Optimization of a Municipal Treatment Plant Using EnviroPro Designer

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The increasingly stringent environmental regulations on discharge standards have rendered the optimal design and operation of industrial and municipal treatment plants a challenging task. The new regulations require tracking and control of VOCs and heavy metals if such chemicals are present in the influent stream. Further, they require more effective removal of nutrients (organic nitrogen, and phosphorus). To address the above issues at our facility, EnviroPro Designer, a comprehensive environmental simulator from Intelligen, Inc., was used to model and analyze our wastewater treatment plant. The work was performed in two phases. In phase one, we developed and validated a model of the existing facility. In phase two, we carried out sensitivity analysis and evaluated a number of process modification scenarios. This paper will describe the findings of our modeling work and our experience from using EnviroPro Designer.

#### INTRODUCTION AND BACKGROUND

The Edward J. Patten Water Reclamation Facility is a  $6.5 \text{ m}^{3}/\text{s}$  (147 mgd) capacity secondary treatment plant located in Sayreville, New Jersey that is owned and operated by the Middlesex County Utilities Authority (MCUA). The MCUA treats the flows contributed by the thirty-three municipalities and nine direct industrial dischargers within its 829 km<sup>2</sup> (320 square miles) service area, making this plant the second largest wastewater treatment plant in the state.

Processing steps at this facility include grit removal, primary treatment, secondary treatment, and chlorination prior to discharge into the Raritan Bay. The resulting biosolids (primary and secondary) are gravity thickened, dewatered on belt filter presses, and stabilized using the patented N-Viro process of advanced alkaline stabilization. The resultant product, Meadow Life, is beneficially used at the county's Edgeboro landfill for cover material, and by the agricultural community as a liming agent and soil conditioner. The plant was constructed in the mid-1970s and for secondary treatment utilizes one of the first high purity oxygen (HPO) activated sludge systems of the UNOX design developed by Union Carbide, Inc. The activated sludge treatment facilities consist of four covered concrete tanks which function as parallel trains. Each train is separated into four stages by concrete baffle walls

and equipped with surface aerators for dissolution of high-purity oxygen in the mixed liquor as required to support biological activity and mixing of tank contents. Process oxygen for this system is generated on site in a 410 tonne (450 ton) per day cryogenic air-separation facility. A flow diagram for this facility is presented on Figure 1.

Wastewater treatment plants are designed to convert untreated liquid wastes into an acceptable final effluent, and to dispose of solids removed from the process. At this plant, solids removed from the wastewater or produced in the secondary system were disposed in the ocean until 1991 when this practice was banned by federal and state laws. The plant was originally designed in the early 1970's with three basic objectives:

 A minimum removal through the plant of 85% of total suspended solids (TSS) and biochemical oxygen demand (BOD5).

A maximum monthly average concentration of 30 mg/l for TSS and BOD5 in the effluent.

3. Pathogen reduction to less than 200 colony forming units per 100 ml.

At the time of plant design and construction, the primary federal legislation affecting wastewater treatment was the Federal Water Pollution Control Act Amendments of 1972 (PL 92-500). The effluent limits described above were technology-based, conventional pollutants, and were a requirement for federal funding. Several revisions to this law have since occurred, beginning with the Clean Water Act of 1977 (PL 95-217) which defined conventional, nonconventional and toxic pollutants, the Construction Grant Amendments of 1981 (PL 97-117), and finally the Water Quality Act of 1987 (PL 100-4) which continued the efforts to address the question of toxics control in discharges to waters, and began to address nonpoint sources of pollution. In addition to these laws, the Clean Air Act Amendments of 1990 directed treatment plants to inventory emissions from their processes, including wastewater streams, combustion sources, and solids handling facilities to determine if they are major sources of air toxics. In 1993 the USEPA promulgated the Part 503 regulations which contain the technical standards for three sewage sludge use or disposal practices: land application, surface disposal, and incineration. These regulations set limits on the amount of heavy metals that can be present in the sewage sludge. As recently as 1996 new limits were placed in the MCUA's discharge permit to regulate the amount of copper and mercury that the plant can discharge into the Raritan Bay, a



Figure 1. Treatment plant flow diagram ...

direct result of the National Estuary Program established by Congress under the Water Quality Act of 1987.

As can be seen, there are increasingly stringent environmental requirements being imposed on existing as well as new industrial and publicly owned treatment works (POTWs). These requirements may at times be in conflict with each other, e.g. increased removal of copper from the liquid stream will increase the level of copper that will be present in the sludge. Federal funding for POTWs to meet new regulations is practically non-existent; reauthorization of the Clean Water Act has been stalled in Congress since 1993. The challenge then, for existing and future treatment facilities, is to design and operate processes in the most efficient and cost effective way. To address the above issues at our facility, EnviroPro Designer®, a comprehensive environmental simulator from Intelligen, Inc. was used to model and analyze our treatment plant.

#### DESCRIPTION

Computer-aided process design tools have been used with success in the chemical process industries for over four decades to facilitate process analysis, evaluation and optimization. The increasing cost and complexity of environmental processes indicates a need for similar computer-aided process design tools. Unfortunately, modeling environmental processes, especially biological wastewater treatment, is a difficult problem since one is dealing with mixed microbial populations, soluble and suspended organic and inorganic compounds with properties that are difficult to predict using thermodynamic and transport phenomena principles. In addition, most modeling work to date has concentrated on kinetic studies based on lumped environmental stream properties (e.g. BOD<sub>5</sub>,COD, TSS) as opposed to biodegradability of individual chemicals present in a multicomponent mixture. Limited work has been done on VOC volatilization, sorption of heavy metals on the sludge, contribution towards effluent toxicity, etc. In addition, most pollutants are present in very low concentrations, thereby requiring accurate material balances that can predict trace contaminant levels.

EnviroPro Designer is an environmental process simulator designed to enhance the productivity of engineers and scientists engaged in the design, development, and assessment of integrated waste recycling, treatment, and disposal processes. Particular emphasis is placed on the requirement to carry out material balances on constituents and predict the fate of hazardous chemicals (e.g. heavy metals, VOCs) in integrated environmental processes. The key features of EnviroPro Designer include:

· Intuitive graphical user interface.

 Complete simulation facilities including mass and energy balances as well as equipment sizing.

- Models for over 40 unit operations used in the environmental and process industries.
- Thorough process economics.
- · Waste stream characterization.

- Rigorous VOC emission calculations from the different treatment units.
- · Chemical component fate prediction.
- Extensive databases of process equipment, chemical components, and construction materials.
- · Process scheduling of batch operations.
- Compatibility with a variety of graphics, spreadsheet and word processing packages.
- · Advanced hypertext on-line help facility.

The general structure of the software consists of the graphical user interface, the process simulation module, and the economic evaluation module. The user builds a flowsheet by selecting equipment from the "Units\_Ops" menu and drawing the material streams that connect the units. All input-output information is provided and displayed through dialog windows.

The process simulation module assists the user to interactively develop and analyze integrated flowsheets for waste recycling, treatment, and disposal processes. Flowsheets consist of unit operations, material streams, and chemical components. A flowsheet can have any number of these objects.

A unit operation object is represented on the computer screen with a picture. For each unit operation, there is a model that describes its performance. The primary function of a unit operation model is to carry out the material and energy balances around a process step and estimate outlet stream variables given inlet stream variables and operating specifications. The user provides engineering information during initialization of unit operations through unit specific dialog windows. Material balances are estimated in a sequential modular approach and, if recycle streams are included, the unit operations that are part of the recycle loop are solved iteratively until the flowsheet calculations converge.

Streams represent the flow of material from one unit operation to the next and are displayed as polylines on the screen. A stream object stores component specific information, such as mass and mole flowrate, weight or mole percentage, stream name, and other properties such as temperature, pressure, density, etc.

Chemical components are used to describe flow and composition of material in streams. EnviroPro distinguishes between conventional components that can be described with thermodynamic models, and non-conventional components, such as biomass, which cannot be satisfactorily modeled with currently available thermodynamic models. The program is linked to a database module that provides access to thermodynamic, environmental (contributions to COD, BOD, TSS, etc.), and regulatory properties (e.g. SARA Title III) for about four hundred chemicals. The user can also add to this database if desired.

#### PLANT SIMULATION EXAMPLE

The following example details the development and validation of the existing wastewater treatment plant. After the different steps in the plant were created, average plant data from January through December 1996 was used as an input to the model. Output values were compared with actual plant results, as well as the composition and flow rates of the various streams, as well as typical operating parameters for the secondary system.\

#### **Process Description**

The influent to the treatment plant enters three grit chambers where sand, and other heavy particles are removed (see Figure 1). After the grit chambers, the influent is joined by two solids recycle streams (TTO-overflow from the gravity thickeners, and Filtrate from the belt presses) forming the primary influent (PI) stream. Solids are removed in the primary settling tanks, creating the first sludge stream (PS), and the primary effluent stream.

#### Table 1. Overall plant performance

		Flowrate	
Component	Influent kg/h	Effluent kg/h	Biosolids kg/h
Ammonia	603	610	0
Biomass	4,025	351	4,681
Diss. Solids	14,000	13,990	10
Dom. Waste	3,866	106	7
<b>Fixed Solids</b>	1,534	14	1,531
Nitrate	52	52	0
Water	20,389,250	20,531,684	20,988
X-vss-I	10	124	660
X-vss-n	100	4	93
Total	20,413,440	20,546,935	27,970

Secondary treatment consists of the oxygenation tanks (four plug flow reactors in parallel) where the biological oxidation of organic materials occurs, and the final settling tanks where the biomass from the reactors is separated from the treated wastewater. The return activated sludge (RAS) is recycled to maintain a certain biomass concentration in the oxygenation tanks. A portion of this return sludge representing daily growth and death of the microorganisms is wasted to the gravity thickeners, the WAS stream. The effluent from the final settling tanks is chlorinated for disinfection, and discharged into the Raritan Bay.

### Table 2. Stream Comparisons

	Fle	owrate	Concentration		
Stream M	lodel m <sup>3</sup> /hr	Actual m3/hr	Model mg/1	Actual mg/1	
Primary Sludge	690	710	7,437	9,372	
Return Sludge	11,153	11,070	8,892	9,658	
Thickned Sludy	ge 159	139	45,060	35,900	
Filtrate	292	276	578	346	

The primary sludge and the waste activated sludge from the secondary system are sent to gravity thickeners where they are mixed and thickened to a solids concentration of 3% w/w. This thickened sludge is dewatered on belt filter presses to a solids concentration of 25% w/w. The resulting biosolids cake is then mixed with quicklime (CaO), and lime kiln dust (LKD) to provide pathogen destruction, and raise solids content to a minimum of 52% w/w. After a three day curing period, the product Meadow Life is ready for distribution to the various markets.

#### Table 3. Overall Plant performance Based on Environmental properties

	Plant Inf	luent	Plant Effl	uen
Component	Model mg/l	Actual mg/l	Model mg/l	Actual mg/l
COD	573	586	136	122
BOD5	190	190	10	14
TS	959	967	705	752
TSS	235	235	17	17
VSS	178	194	15	16
TDS	724	685	687	672
TKN	50	39	26	30
NH <sub>3</sub>	40	30	20	26
NO <sub>3</sub> /NO <sub>2</sub>	2	3	2	4
Total P	4	4	0	2

Con	nponent	Model	Actual	
ML	SS (mg/l)	2,930	2,820	
ML	/SS (mg/l)	2,585	2,450	
Slud	ge Age (hr)	100.2	86.4	
F/M	(kg/kg)	0.47	0.5	
Recy	cle Rate (%)	53.5%	53.1%	
(m <sup>3</sup> /	hr)	10,930.0	10,833.0	
02	Use (kg/hr)	5,387	4,129	

The average input to the facility as entered into the model is presented in Table 1. The Biomass component represents active heterotrophic organisms, Dom. Waste is the organic, biodegradable substrate, X-vss-I are inert solids (dead biomass), X-vss-n are nitrifying organisms (autotrophic biomass), Diss. Solids are total, non-biodegradable solids such as salts, etc. The effluent and biosolids results are the output of the model.

Table 2 presents the actual values and the model results from several streams within the plant.

The difference in concentration for the thickened sludge can be attributed to very poor performance by the plant's thickeners during the summer months which lowers the annual average During the other months, the actual results are in line with the concentration predicted by the model.

Table 3 presents the overall plant performance characteristics as calculated from the model, and compares them to the actual plant data. As can be seen, the simulation results are in good agreement with the plant data. Also note that BOD and TSS are the materials which are readily removed, as they were the basis of design for the original plant; some nutrient removal occurs, however it is not a significant amount.

Table 4 summarizes typical operating data from the secondary system. Again, there is good correlation between the predicted values and the actual plant operating data. Once the model of the existing wastewater plant was validated, several process scenarios were created dealing with particular components such as metals, VOCs, and nutrients.

#### NON-CONVENTIONAL POLLUTANTS EXAMPLES

As more limits are placed on treatment plants, the fate of the numerous pollutants entering the facility must be determined. Conventional pollutants will be removed by the plant as originally designed, however, non-degradable compounds will be partitioned between the liquid effluent stream and the biosolids stream. Furthermore, some compounds such as VOCs will be present in the air and may be subjected to biodegradation, pass-through, and/or sorption onto the biosolids.

#### Table 5. Copper Loading Matrix

Scenario	Average Condition	State Limit on Sludge	Cur. Limit on Effluent	Fed. Limit on Sludge
Influent Load(kg/hr)	1.9	5	6.9	15
Effluent Conc. (mg/l)	0.015	0.05	0.069	0.15
Effluent Load (kg/day)	7.3	24.7	33.8	74.4+
Biosolids Conc. (mg/kg)	230	565	783*	1,440

\*Current limit on sludge is exceeded

+Current limit on the effluent loading is exceeded

#### Table 6. Toluene Removal

Treatment Step	Emission Rate kg/h	Mass Balance kg/hr
Grit Chamber	0.00018	Influent 106.0
Primary Settling Tanks	0.08397	Effluent 0.5133
Oxygenation Tanks	0.90294	Emissions 0.9900
Final Settling Tanks	0.00083	Biosolids 0.0104
Gravity Thickeners	0.00333	Degraded 104.5
and the second second second		e

#### **Heavy Metals Example**

As was described previously, the treatment plant has recently received a permit limit for copper on its discharge. The maximum daily loading currently allowed in the effluent is 34 kg/day. In addition, the resulting biosolids must also be below a certain level to be safely land-applied. Under New Jersey law, the resulting sludge cake must have a maximum copper concentration of 600 mg/kg dry weight to be land-applied. New federal regulations which are expected to be adopted by New Jersey will raise that concentration to 1,500 mg/kg dry weight. The effect of different quantities of copper entering the treatment plant were studied with the model. As with the conventional pollutants, an initial calibration was performed with actual plant data, and the model was adjusted to reflect the actual results. Table 5 presents the outcome of these various scenarios on the effluent and the biosolids streams.

Thus, an influent loading in the range of 1 to 5 kg/hr will produce an acceptable biosolids product within the state limit, and will not violate the effluent load limit. If the new federal sludge limit is applied, the amount of copper that can be tolerated in the sludge will lead to a violation in the effluent loading. Therefore, the federal sludge limit will allow more copper to be received at the plant but the effluent loading parameter will then become the limiting factor. One should also note that copper concentrations throughout the treatment plant are also available. For example, the model predicts, under average conditions, a copper concentration of 1.3 mg/l in the return sludge; a sample of the return sludge analyzed in 1986 had a copper concentration of 1.5 mg/I under similar influent and effluent concentrations. Furthermore, one can vary the physical form of the metal, dissolved vs. attached to biomass, and observe its removal through the plant.

#### Volatile Organic Compound Example

While treatment plants have been regulated on their liquid and solid discharges, they are also considered a major source of air pollutants. As a result of the Clean Air Ammendments of 1990, New Jersey has established May 15, 1998 as the deadline for submission of Title V Operating Permits for wastewater treatment plants. Any facility which has the potential to emit a hazardous air pollutant (HAP) equal to or exceeding 10 tons per year, or 25 tons per year of any combination of HAPs will need an Operating Permit. Therefore, an emission rate of approximately 1 kg/hr for any HAP will force the facility to install reasonably available control technology (RACT) to reduce the amount of the HAP emitted.

EnviroPro Designer was used to study the fate of one HAP (toluene) through the treatment plant, and to identify the steps where most of the volatization occurs. Table 6 presents the results of this evaluation.

Two things are apparent from Table 6:

• 98.5% of the toulene is biodegraded.

 Significant resources will have to be expended to control emissions from the various treatment steps. Currently only the oxygenation tanks and gravity thickeners are covered, the remaining tanks represent an approximate surface area to enclose of 39,500 m<sup>2</sup> (



FIGURE 2. Nitrogen removal flow diagram.

425,000 ft<sup>2</sup>, approx. 10 football fields). The cost to cover the thickeners (2,860 m) was approximately \$ 3.0 million, and these monies would be expended to control less than 1% of the influent load to the plant. Is this a wise use of limited resources?

#### Nutrient Removal Example:

Although the treatment plant is not currently required to remove nutrients, the Comprehensive Conservation and Management Plan for the New York/New Jersey Harbor Estuary Program has identified eutrophication, or the excessive enrichment of a waterbody by nutrients and organic materials, as a problem in the Harbor and Long Island Sound. This plan has identified nitrogen as the limiting nutrient in the Harbor with municipal point sources (POTWs) as the dominant source of the total nitrogen load to the Harbor. It is very likely that, within the next ten years, the treatment plant will be required to remove nitrogen.

The control of nitrogen in wastewater begins with nitrification for oxidation of ammonia-N and, if required, ends with denitrification for reduction of nitrates and nitrites to nitrogen gas. Both steps may be accomplished biologically. Biological nitrification can be accomplished by suspended-growth or by attached-growth systems. The two-step process begins with ammonium conversion to nitrite by Nitrosomonas bacteria, which is followed by nitrite conversion to nitrate by Nitrobacter bacteria. The relatively slow growth rate of Nitrosomonas bacteria limits the nitrification process. Both organisms are most efficient at temperatures of 30 to 36°C, pHs of 8.0 to 8.5, and dissolved oxygen of 2.0 mg/I. It is therefore imperative that the sludge age be long enough to allow maintenance of the nitrifying organisms; at least five days and substantially more under conditions of reduced temperatures. Denitrification by a suspended-growth system is comprised of an anaerobic reactor equipped with mixers, and a settling tank with provisions for recycle.

Figure 2 depicts a possible schematic for nitrogen removal at the MCUA facility. As can be seen, a substantial increase in tankage would be required to accomplish this task. The number of oxygenation tanks is tripled, and in addition, 18 new reactors of approximately the same size as the oxygenation tanks would be required. Table 7 depicts the effluent that could result from this facility.

#### **Table 7. Nitrogen Removal Results**

	Plant Influent	Plant Effluent	Plant Effluent
Component	Model mg/l	Model mg/l	w/o N removal mg/l
COD	573	24	136
BODs	190	10	10
TS	959	705	705
TSS	235	17	17
VSS	178	15	15
TDS	724	687	687
TKN	50	2	26
NH <sub>3</sub>	40	2	20
NO <sub>3</sub> /NO <sub>2</sub>	2	45	2
Total P	4	0	0

Additional modifications must be done to this design since a large amount of nitrates are still discharged. Intermediate settling tanks and recycle streams would be required. Also, one could add synthetic prepatations of nitrifying and denitrifying organisms to reach the desired levels with fewer tanks. However, any alternative will require significant umounts of money, therefore, a careful evaluation of the various routes is mandatory. A tool such as EnviroPro Designer can be utilized to nartow the number of choices, as well as to optimize the design and operation of the final choice, and evaluate the associated costs.

#### Conclusions

Process simulators have been used in the chemical industries for over forty years to facilitate process analysis, economic evaluation, and optimization with a high degree of success. In the last few years similar tools have become available for wastewater treatment and other pollution control processses. The various features of a comprehensive environmental simulation and design tool have been presented. EnviroPro Designer can be used to model on a computer the various steps of a modern wastewater treatment plant. It can be used to predict the treatability, and track the fate of individual chemicals such as heavy metals, solvents, and VOCs, performing rigorous mass and energy balances. In addition, EnviroPro Designer can also present these components in the more traditional environmental language (TSS, BOD, COD). This package can also be used to analyze, evaluate, and optimize plant expansions and modifications to meet increased throughput or changing regulations. EnviroPro Designer can carry out economic evaluations and estimate capital and operating costs of treatment plants. Consequently, it can be used to rationally estimate and justify processing fees on existing processes, or estimate the cost and impact of additional treatment steps.

The use of EnviroPro Designer, like other software tools, requires a new way of thinking. The examples provided have illustrated the powerful capabilities of this package, however, one must remember that simulation is an attempt to approximate the behavior of the real world, and should not be a substitute for research and good engineering. Tools such as EnviroPro Designeri'a8 can aid engineers to design and operate processes within vanous environmental constraints. They can also be used to show the impact of process changes or the cost and benefit of new regulations. Ultimately, these tools can increase the knowledge and understanding level of the user, and may contribute to significant advances in the field.

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## Evaluating Acids and Chelating Agents for Removing Heavy Metals from Contaminated Soils

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The prevalence of beavy metal soil contamination at Army facilities poses a serious threat to human health and the environment. To address this problem, the US Army Engineer Waterways Experiment Station in Vicksburg, MS is developing a mobile pilotscale soil washing treatment facility that can be used to remove metals from the contaminated soils. To support this project, laboratory studies were conducted on both acids and chelating agents to evaluate their ability in extracting beavy metals from contaminated soils. Eight soils contaminated with lead, cadmium, and chromium were selected for use in this study. Contaminant concentrations in the various soils ranged from 4,000-30,000 mg/kg lead, 40-1,000 mg/kg cadmium, and 500-2,000 mg/kg chromium.

The results indicated that, before a full-scale clean-up is initiated, a preliminary investigation is needed to determine principal contaminants of concern, their concentrations, and soil type followed by treatability studies to determine optimal reagent and concentrations of reagents for cleanup. Specific results from this study also indicated that Cd was the easiest metal to remove from soils followed by Pb and Cr. The results also suggested that the strong acids and chelating agents were both effective extracting agents, and the latter group of compounds may be more useful in soil washing because they are less harmful to the soil environment. Finally, higher initial concentrations of metal contaminants in the soil resulted in greater metal removal efficiencies using the reagents.

#### INTRODUCTION

Thousands of sites in the United States have been heavily polluted with organic and inorganic contaminants resulting from various activities including electroplating, metal working, ammunitions manufacturing, battery recycling, chemical processing, solvent manufacturing, etc. Many of these sites are current or formerly used federal facilities. The hazardous substances contained in the soil and water at these facilities require remediation to avoid further environmental degradation. Among the major contaminants of concern at many federal facilities are heavy metals, which can be found at facilities with operations including firing ranges, ammunition manufacturing facilities, and open burning pits. In fact, heavy metals currently constitute five of the six most cited hazardous materials at Army sites [1]. The three most prevalent metals at these sites are lead (Pb), cadmium (Cd), and chromium (Cr). All of these metals are potentially toxic to human health and can cause a variety of ailments including brain/neurological damage, liver and kidney damage, and cancer. Contaminant pathways include ingestion, absorption through the skin, and dust/vapor inhalation [2,3].

#### Soil Washing Technology

To combat such threats to human health, a limited number of technologies have been developed for treating and/or disposing of soils contaminated with heavy metals. Soil washing is one such emerging technology currendy being evaluated for the removal of heavy metals from contaminated soils. Soil washing employs both physical and chemical methods to reduce the contaminated soil volume and remove the heavy metals from the soil. Physical separation processes separate soil into fractions having differences in particle size, density, and/or surface area. Metals can be present in soil as either particulate or sorbed contaminants. Particulate (or elemental) metals can generally be present in any soil fraction while complexed metals resulting from metal dissolution are typically concentrated in the fines fraction of the soil. Since heavy metals are generally partitioned onto the finer particles of the soil, the volume of soil to be treated chemically can be largely reduced through the use of physical separation processes.

Two major classes of extractants include acids and chelating agents (chelates), which are capable of desorbing heavy metal contaminants from soil into solution. Acid extraction capitalizes on ion exchange and soil matrix dissolution to solubilize metals. Although acids effectively increase the solubility of metals, strong acids may destroy the basic structure of the soil, thus leaving it unsuitable for revegetation [1]. Some of the most common acids used for leaching heavy metals from soils include nitric acid (HNO<sub>3</sub>) and hydrochloric acid (HCI). Chelating agents can be more environmentally benign compounds and contain varying numbers of functional groups or binding sites that are capable of complexing heavy metals. When contacted with metals bound to soil particles, the sites on the chelating agents bind with the metals that are sorbed to the soil. A net solubilization of the metal occurs when the metal has a greater affinity for chelation than soil attachment [4]. Typical chelating agents include ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA), and citric acid.

#### **Previous Studies**

Several studies have attempted to optimize the metal extraction process using a variety of chelating agents. Peters et al. has done extensive research on the complexation of metals through the use of chelating agents [5]. The majority of their testing focused on Pb removal using EDTA and NTA. Their experiments utilized uncontaminated clay/silt soil spiked with 500-10,000 ppm Pb and mixed with EDTA and NTA using concentrations ranging from 0.01 M to 0.1 M over the pH range 4-12. Peters et al. results indicated that Pb recovery using EDTA generally exceeded 60%, regardless of EDTA solution concentration, initial contaminant concentration in the soil, or pH. In general, Pb extraction using NTA was ineffective, removing only a maximum of 19% in the pH range 4-12.

Elliott and Brown have also conducted comparative studies to evaluate the metal extraction capabilities of EDTA and NTA [6]. Their study focused on the percent removal efficiency of the two chelating agents when mixed with a contaminated soil from a former battery recycling facility that contained 211,000 mg/kg Pb. Comparing EDTA and NTA concentrations from 0.01 M to 0.08 M over a pH range of 4-12, Elliott and Brown found that, given equal concentrations of reagents, EDTA was generally a more effective extracting agent than NTA because the stability constant of Pb-EDTA<sup>2-</sup> (18.0) is much greater than that of Pb-NTA-(11.4). Pb removal efficiency of EDTA ranged from about 35% at pH=10.5 and a concentration of 0.02 M to approximately 95% at pH=4 and a concentration of 0.08 M. Pb extraction using NTA ranged from about 11% at pH=11.5 and a concentration of 0.01 M to roughly 63% at pH=10 and a concentration of 0.06 M. The researchers also studied the effects of electrolyte addition by mixing 0.5 M NaClO<sub>4</sub> into the EDTA and NTA solutions. Their results showed that Pb removal increased 10% using EDTA along with NaClO<sub>4</sub> while Pb recovery dramatically decreased using NTA with NaClO<sub>4</sub>.

A number of studies have also been conducted to determine the metal extraction efficiency of acids including HNO<sub>3</sub> and HCl. One such study was performed by Mortazavi et al. on a <1.8 mm size soil fraction initially contaminated with various metals including 12,600 mg/kg Pb and 30 mg/kg Cd [7]. Their results indicated that HNO<sub>3</sub> was a more efficient extracting agent than HCl for the removal of Pb. Approximately 66% of Pb in the soil was removed using 0.1 N HNO<sub>3</sub> compared to only 33% Pb removal using 0.1 N HCl. However, 0.1 N HCl removed nearly 54% of Cd in the soil while 0.1 N HNO<sub>3</sub> removed only 39% of Cd.

Neuhauser et al. also investigated the metal extraction capability of

	TABLE 1. Selected Soils for Testing										
Site	Location	Soil Type	Contaminant								
LAAP Site 1	Shrevport, LA	Sand: 77% Silt: 15% Clay: 8%	Chromium (550 mg/kg)								
LAAP Site 2	Shrevport, LA	Sand: 74% Silt: 19% Clay: 7%	Chromium (1,400 mg/kg) Cadmium (40 mg/kg)								
Fort Ord	Monterrey, CA	Sand: 89% Silt: 8% Clay: 3%	Lead (4,750 mg/kg)								
SE Fort Site 5-8	Louisiana	Sand: 72% Silt 10% Clay: 18%	Lead (30, 350 mg/kg)								
SE Fort Site 10	Louisiana	Sand: 24% Silt: 40% Clay: 36%	Lead (6,300 mg/kg)								
SE Fort Site 12	Louisiana	Sand: 56% Silt: 8% Clay: 36%	Lead (21, 650 mg/kg)								
Umatilla Army Depot	Hermiston, OR	Sand: 68% Silt: 24% Clay: 8%	Lead (15, 150 mg/kg)								
WES Spiked Soil	Vicksburg, MS	Sand: 5% Silt: 95% Clay: 0%	Chromium (3,000 mg/kg) Cadmium (950 mg/kg) Lead (6,800 mg/kg)								

LAAP = Louisiana Army Ammunition Plant; SE Fort = Undisclosed Site

HCl [8]. Their results indicated that 1.0 M HCl was an effective extracting agent for the removal of heavy metals from an anaerobic sludge containing 735 ppm Pb, 96 ppm Cd, and 1,949 ppm Cr. Overall, 1.0 N HCl removed 66% of Pb, 68% of Cd, and 56% of Cr from the sludge.

A variety of other chemical compounds have been evaluated as metal extracting agents. The U.S. Bureau of Mines (USBM) has successfully used fluorosilicic acid to leach 99% of Pb from spent battery casings [9]. Assink [10] determined that highly basic sodium hydroxide (NaOH) disperses metal contaminants during extraction, especially those contaminants in the clay or humus soil fractions. Thus, NaOH may also be a useful extracting agent.

#### MATERIALS AND METHODS

This study examined the heavy metal removal efficiency of several extracting agents in treating a wide variety of clayey and sandy contaminated soils. Using concentrations of 0.01 M, 0.05 M, and 0.1 M, the selected extracting agents included: HNO<sub>3</sub>, HCl, fluorosilicic acid, citric acid, EDTA, DTPA, NTA, and NaOH. This selection of reagents and the range of concentrations was based on the review of previous metal extraction studies.

A wide variety of soils from across the United States were selected for use in this study. One of the criteria for selection focused on the predominant soil type: sand, silt, or clay. Other key selection criteria centered on the contaminant found in the soil matrix and the concentrations of the metals present. The selected soils, their location, soil type, and predominant contaminant are listed in Table 1. The particle size distribution into sand, silt, and clay fractions for each of the soils was determined using a basic hydrometer method analysis outlined by Tan [11]. These results are also listed in Table 1.

#### Soil and Solution Preparation

Each of the selected bulk soils found in Table 1 was thoroughly dried and homogenized using a Gilson® Sample Splitter. The bulk samples were sieved to less than 2 millimeters and a 500 ml sample was drawn from this sample for use in the extraction tests. Solution preparation consisted of dissolving crystal or concentrated forms of the acids, chelating agents, and base in distilled, deionized water (DDI). The following compounds were used to make the solutions: HCl (reagent grade), HNO<sub>3</sub> (reagent grade), fluorosilicic acid as 25% weight in solution with water, citric acid (99% pure), NTA disodium salt (99% pure), EDTA calcium disodium salt hydrate (98% pure), DTPA calcium trisodium salt hydrate (97% pure), and NaOH. All solutions were prepared using Kimax® Class A volumetric flasks.

#### **Total Metals Analysis**

To determine the total metals concentration in each of the soils prior to extraction testing, samples from each of the selected soils were thoroughly riffled and mixed in an attempt to obtain homogeneity. The samples were digested according to EPA Method 3051 [12]. Total metals samples were analyzed using a Perkin-Elmer® Model 5100PC atomic absorption spectrophotometer (AAS) using EPA Method 7000A [12]. Each sample was digested and analyzed in triplicate, and an average was taken to determine the total metal content of each sample.

#### **Extraction Testing**

Five grams of each soil sample was weighed using a top-loading balance accurate to  $\pm$  0.01 g and placed in a 250 ml Nalgene® high density polyethylene (HDPE) bottle. To meet a recommended solid-to-liquid ratio of 0.05 as determined from previous studies [13], 100 ml of extracting agent was added to the 250 ml bottle containing the soil. Each of the samples was placed in an end-over-end tumbling apparatus operating at 18  $\pm$  2 rpm for 30 hours to insure that chemical equilibrium was reached [13]. After tumbling, the samples were placed in a Sorvall® Superspeed SS-3 table-top centrifuge. Each sample was centrifuged for 30 minutes at approximately 15,000 rpm after which the liquid portion of the sample was decanted into a 125 ml Nalgene® HDPE bottle. The concentration of dissolved metal in each sample was then determined using a Perkin-Elmer® Model 5100PC AAS using EPA Method 7000A [12]. Due to the large number of samples being tested, no replicates were run.

#### Calculations

To determine the percent removal efficiency of each of the solutions, the following calculations were used:

(1) Calculate mg of dissolved metal in extract per gram of soil used in the test.

$$\frac{mgMe_{diss}}{g\ Soil} = \frac{\left(\frac{mg}{L}\ Dissolved\ metal\right)x\left(\frac{1L}{1000\ ml}\right)}{(5g)}$$

(2) Calculate mg of total metal per gram of bulk soil used in the test.

$$= \frac{mgMe_{total}}{g \ Soil} = \left(\frac{mg}{kg} \ Total \ metal\right) x \left(\frac{1kg}{1000 \ g}\right)$$

(3) Calculate percent removal.

% Removal = 
$$\frac{mgMe_{diss} | g Soil}{mgMe_{total} | g Soil} x 100$$

#### **RESULTS AND DISCUSSION**

As evidenced in the previous studies, the range of metal removal efficiencies varies with the metal contaminant, type, concentration, and pH of extracting agent, initial metal concentration in the soil, and soil type. As a result, each of these factors was considered in the batch studies.

#### Effect of Contaminant Type and Reagent Selection Pb-Contaminated Soils

Six of the selected soils, including the SE Fort Site 10, SE Fort Site 12, SE Fort Site 5- 8, Umatilla, Ft. Ord, and WES Spiked soils, contained high concentrations of Pb and were mixed with three concentrations of each of the extracting agents. Average Pb removal efficiency over the range of test soils and reagents is presented in Figure 1. Extraction efficiencies for each individual soil, reagent, and concentration may be found in Table 2.

The results clearly indicate that both acids and chelating agents were much more effective at extracting Pb than NaOH, regardless of the concentration tested. Pb contained in these soil matrices was therefore not very soluble at



FIGURE 1. Average Pb removal results using each extracting agent.

**TABLE 2. Metal Removal Efficiency Versus Extracting Agents** 

Extractant	Conc.	SE Fort 10 (Pb)	SE Fort 12 (Pb)	SE Fort 5-8 (Pb)	Umatilla (Pb)	Ft. Ord (Pb)	WES Spk (Pb)	LAAP Site 2 (Cd)	WES Spk. (Cd)	LAAP Site 1 (Cr)	LAAP Site 2 (Cr)	WES Spk (Cr)	
HNO <sub>3</sub>	0.01M	55.1	99.0	97.4	8.6	• 46.4	0.1	16.2	91.1	20.3	0	0	
HC1	0.01M	99.0	66.9	62.8	1.5	85.9	0.3	32.4	82.9	15.9	0	0	
Acid	0.01M	3.8	91.6	50.9	26.7	57 3	147	86.5	99.0	9.8	13.0	20.6	
Citric Acid	0.01M	29.5	29.0	14.7	46.2	16.1	45.0	64.9	88.5	26.8	25.8	4.7	
EDTA	0.01M	14.5	30.9	49.4	13.6	17.1	80.5	75.5	99.0	14.5	0	0.3	
DTPA	0.01M	17.0	78.9	99.0	52.9	32.3	99.0	86.5	99.0	0	0	0	
NTA	0.01M	14.0	99.0	99.0	99.0	51.4	83.4	91.9	99.0	26.8	2.4	0.9	
NaOH	0.01M	0.1	0.1	0.4	0.3	1.8	0	0.6	0	16.6	0.3	0	
HNO <sub>3</sub>	0.05M	99.0	99.0	99.0	99.0	99	7.9	99.0	99.0	28.6	24.9	0	
HC1	0.05M	36.3	99.0	99.0	99.0	78.1	28.2	99.0	99.0	23.5	22.4	0	
Fluorosilici	ic												
Acid	0.05M	37.7	99.0	99.0	99.0	89.9	99.0	99.0	99.0	34.7	57.8	99.0	
Citric Acid	0.05M	17.1	64.7	43.2	46.6	32.4	76.1						
99.0	99.0	28.6	59.1	33.7									
EDTA	0.05M	9.6	56.3	51.7	23.9	26.5	95.9	32.4	97.0	16.3	0.1	0.6	
DTPA	0.05M	35.5	84.1	99.0	74.0	26.9	99.0	5.9	99.0	41.2	0	0	
NTA	0.05M	11.7	99.0	99.0	15.5	85.6	99.0	99.0	99.0	32.9	10.8	2.6	
NaOH	0.05M	0	14.0	41.2	14.1	9.3	3.3	0	0	50.6	0	0	
HNO <sub>3</sub>	0.1M	35.4	99.0	99.0	99.0	27.4	36.2	99.0	99.0	29.3	58.3	0	
HCI	0.1M	58.5	99.0	99.0	99.0	49.5	47.4	99.0	99.0	0	54.5	0.4	
Fluorocilic	ic										6.006		
Acid	0.1M	8.3	99.0	99.0	99.0	37.7	99.0	99.0	99.0	50.6	99.0	99.0	
Citric Acid	0.1M	99.0	99.0	68.6	99.0	37.6	99.0	99.0	99.0	29.3	74.1	62.6	
EDTA	0.1M	42.4	83.3	85.7	35.9	21.0	99.0	97.3	99.0	0	0	0	
DTPA	0.1M	99.0	16.9	99.0	93.9	18.9	99.0	59.5	99.0	6.1	0.7	2.6	
NTA	0.1M	10.7	99.0	99.0	99.0	26.7	48.3	99.0	90.6	28.2	16.5	3.8	
NaOH	0.1M	3.0	52.4	89.1	33.8	14.7	11.8	0	0	18.1	0	0.8	

high pH (>11). For the strong acids including HNO<sub>3</sub>, HCl, and fluorosilicic acid, a significant increase in extraction efficiency occurred as the concentration increased from 0.01 M to 0.05 M; however, this same trend did not hold as the concentration was further raised to 0.1 M. The latter result was somewhat surprising since the net solubilization of heavy metals generally increases in stronger acids.

This phenomenon may be explained by investigating the changes in pH of a particular system. For example, in the representative  $HNO_3$ . Umatilla soil extraction system, the initial pH of the 0.01 M  $HNO_3$  solution was approximately 2.2. After addition to the soil, the system pH increased to 5.3 as a result of the soil's buffering capacity. At this higher pH, only 8.6% of the Pb was recovered in solution (see Table 2). Upon addition of 0.05 M  $HNO_3$ , the final system pH dropped to 2.0. At this lower pH, 99% of the Pb was removed from the soil. Subsequently, an increase to 0.1 M concentration only decreased the system pH to 1.6 and did not further enhance recovery.

The chelating agents were also effective at removing Pb from the soils. Increased Pb recovery was observed with each increase in concentration for both citric acid and EDTA. Extraction efficiency was generally unaffected by a change in concentration in DTPA and NTA. Unlike the mineral acids, lower system pH typically leads to the protonation of the ionized chelate species. The drop in pH results in competition for binding sites between the hydrogen and metal ions, which results in a net decrease in metal solubilization. In fact, EDTA will begin to precipitate out of solution when the pH drops below 2.5 [14]. Therefore, chelating agents (unlike mineral acids) can be successful extracting agents even at neutral to alkaline pH's. In these studies, the

typical extraction system pH's for citric acid, EDTA, DTPA and NTA were approximately 2.5, 9.5, 9.5, and 8.5, respectively.

#### **Cd-contaminated** Soils

Two of the selected soils contained elevated levels of Cd and were contacted with each of the reagents to evaluate Cd removal efficiency. The average results of these extractions are presented in Figure 2, and the individual removal percentages may be found in Table 2.



Figure 2. Average Cd removal results using each extracting agent.



FIGURE 3. Average Cr removal results using each extracting agent.

The results illustrate that Cd was easier to remove from soils than Pb over the range of extracting agents and concentrations tested. The acids and chelating agents were similarly effective in removing Cd from the soils, and both outperformed NaOH. As in the Pb extraction studies, increasing the strong acid concentration from 0.01 M to 0.05 M enhanced Cd extraction while an increase in concentration from 0.05 M to 0.1 M typically had less impact. An increase in chelating agent concentration from 0.01 M to 0.05 M enhanced Cd extraction using citric acid and NTA while the average extraction efficiency actually decreased significantly using EDTA and DTPA. This decrease in average removal efficiency can be attributed to only the LAAP Site 2 soil, since extraction results from the other Cd-contaminated soil (WES Spiked) did not show a decrease in efficiency with an increase in concentration from 0.01 M to 0.05 M (see Table 2).

#### **Cr-contaminated Soils**

Three of the selected soils were contaminated with Cr and extracted with each of the extracting agents. The average results from these tests are presented in Figure 3, and the individual soil-reagent extraction efficiencies are shown in Table 2.

Unlike Pb and Cd, Cr proved much more difficult to extract from the soils. Only two of the reagents, fluorosilicic acid and citric acid, were able to extract significant quantities of Cr from the soils. A steady increase in extraction efficiency for both of these reagents was observed as the concentration increased from 0.01 M to 0.05 M and from 0.05 M to 0.1 M. The difficulty in removing Cr using this suite of reagents may be attributed to the fact that the majority of the metal was in the less soluble trivalent (+3) oxidation state in all three soils. Improved removal efficiency or solubilization may require the addition of a strong oxidizing agent to convert the Cr<sup>+3</sup> to the more soluble Cr<sup>+6</sup> oxidation state.

Figure 4 presents a E<sub>H</sub>-pH diagram for Cr using HSC Chemistry for Windows [15]. Based on this diagram, we see that in the area of water stabili-



FIGURE 4. EH- pH digram for selected Cr species.

ty Cr (dashed lines) is soluble over the entire range of pH in the hexavalent forms of HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup>; however, it is only soluble under oxidizing conditions. In the pH range of 0-6, the necessary redox potential for efficient Cr solubilization ranges from approximately 650 mV to 1,250 mV. The measured redox potentials of the extraction systems ranged from approximately 100 mV to 700 mV. In most cases, the extracting agents were unable to adequately oxidize the Cr in the soil and bring it into solution. For example, using the HNO<sub>3</sub>-LAAP Site 1 extraction test, the redox potentials of the sluried solution for 0.01 M, 0.05 M, and 0.1 M HNO<sub>3</sub> were 609 mV, 653 mV, and 679 mV, respectively and the pH values were 2.4, 1.6, and 1.4, respectively. According to the stability diagram, maximum solubilization was not reached because the systems were not sufficiently oxidized.

#### **Effect of Initial Metal Concentration**

This study also attempted to examine extraction efficiency coupled with the initial metal concentration in the soils. The Pb-contaminated soils were separated into those containing greater than 10,000 mg/kg and those containing less than 10,000 mg/kg of Pb. Cd-contaminated soils were separated at 500 mg/kg while Cr-contaminated soils were divided at 1,000 mg/kg. Average removal efficiency based on initial metal concentration is provided in Table 3. The results presented in Table 3 indicate that extraction efficiency does depend on initial contaminant concentration for the removal of Pb and Cd. Greater removal of the metals (-20%) was observed in the soils containing the higher initial concentrations of Pb and Cd (greater than 10,000 mg/kg and 500 mg/kg, respectively). This trend may signify that the metals found in soils with smaller total metal concentrations may be more tightly bound in the soil, and therefore may be more difficult to extract. Contrary to the Pb and Cd results, there was very little difference in the extraction efficiencies of those soils containing greater than 1,000 mg/kg Cr versus those containing less than 1,000 mg/kg.

#### Effect of Soil Type

The effect of soil type on metal extraction efficiency was also investigated. As illustrated in Table 1, the six Pb-contaminated soils were classified as pre-

	TABLE 3. Co	omparison of Ex	traction Efficiency	vs. Initial Metal C	oncentration	
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Metal Contaminant	Initial Concentration (mg/kg)	No. of Soils	% Removal at 0.01M	% Removal at 0.05M	% Removal at 0.1M	% Removal Average
Pb	>10,000	3	51	72	85	69
	<10,000	3	36	51	47	44
Cd	> 500	1	82	86	86	85
	< 500	1	57	67	81	68
Cr	>1,000	2	4	20	30	18
	<1,000	1	16	20	26	21

Soil Type	No. of Soils	% Removal at 0.01M	% Removal at 0.05M	% Removal 0.1M	% Removal Average
Sand	3	43	65	68	58
Clayey Sand	1	62	77	81	73
Silt	1	40	64	67	57
Mixture	1	29	31	45	35

#### TABLE 4. Average Pb Extraction Based on Soil Type

dominantly sand, silt, or clay (>65% in one fraction). A comparison of the Pb removal efficiency based on soil type is provided in Table 4. The removal efficiencies are based on average removal using all eight extracting agents. As shown in this table, Pb removal efficiency was significantly greater in the clayey sand material than in the predominantly sand or silt soils. Also, extraction of Pb from soils dominated by only one or two soil types was much greater than Pb extraction from the lone soil that had a fairly even distribution between sand, silt, and clay particles. The difference in removal efficiency between the sand and clayey sand soils contradicts theoretical prediction which indicates that the Pb should be more difficult to remove from clayey soils than from those soils containing mostly sand. Clay materials typically have a greater concentration of organic or humic material which contains functional groups that can tightly adsorb the metal and make it difficult to remove. Also clay soils can physically trap the metals in their interior pore spaces, and these trapped contaminants may not be easily reached by the reagent [16]. Both Cd and Cr removal efficiencies were relatively similar, regardless of soil type.

#### CONCLUSIONS

The results of this study indicated that the extraction of heavy metals from contaminated soils is a function of the type of contaminant, the concentration and pH of extracting agent, the initial metal concentration in the soil, and soil type. Based on these findings, treatability studies should typically be conducted on heavy metal contaminated material before initiating a full-scale soil washing remediation process. Such studies will assist in accessing the most effective extractant and extractant concentration for a particular contaminated soil and will also help to identify soil and extractant interactions.

Specific results from the study showed that Cd was easier to remove than Pb, and both metals were much more soluble than Cr. This result suggests that treating soils contaminated with Cr in the trivalent state may not be necessary since the leachability of the metal may be minimal. However, some type of risk assessment analysis must be performed to determine the ultimate hazard associated with this contaminant. The study also suggested that both strong acids with very low pH and chelating agents with near neutral to alkaline pH were effective extracting agents for the removal of heavy metals. Strong bases with very high pH such as NaOH were not effective metal extractants. Since removal was comparable among the strong acids and chelating agents, the latter class of reagents may be more suitable for full-scale soil washing processes because these chemicals are more environmentally benign and they also have regeneration potential. Furthermore, extraction of the majority of the leachable fraction of Pb, Cd, or Cr in soils may be accomplished with concentrations less than 0.1 M, although batch studies on the actual soil to be remediated will yield the optimal concentration of reagent.

Also, the results indicated that lower initial soil concentrations of Pb (<10,000 mg/kg) and Cd (<500 mg/kg) resulted in lower removal efficiencies over the range of extracting agents. The results regarding the effect of soil type on metal removal efficiency were inconsistent and did not clearly show that metals can be more easily extracted from one soil type versus another. Further batch studies using a broader range of

soils and soil types will be needed to draw definitive conclusions on the effect of soil type on metal extraction.

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# Rapid Evaluation and Installation of a Low Cost Water Treatment Scheme at a Superfund Site

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Wastewater treatment technologies were evaluated for a Superfund Site located in the southern United States to pretreat approximately 3 million gallons of on-site contaminated water to meet POTW pretreatment requirements. A low cost water treatment scheme was developed, designed, installed, and the contaminated water was successfully treated in a 16 week period. The Site included two earthen ponds containing hazardous sediments to be dredged and remediated, and water, contaminated with organics, oil and grase (O&G), and heavy metals. A four week, on-site investigation was conducted to characterize and quantify pond contents and develop a cost-effective, rapid method of treating the contaminated pond water. Rapid installation and start-up of the selected treatment technology was required to meet the pond closure schedule.

#### INTRODUCTION

The treatment technologies evaluated included advanced chemical oxidation, metals precipitation, air stripping, and granular activated carbon (GAC) adsorption treatment. Based on the treatability study results, a treatment scheme consisting of metals and O&G removal, air stripping, and GAC adsorption polishing was selected. The treatment system was designed and the installation was completed five weeks after the conclusion of the treatability study. The metals/O&G removal system consisted of a pH adjustment tank, a flocculation tank, and three settling tanks. To reduce equipment procurement, delivery and installation time, and project cost, on-site equipment was retrofitted when possible. An existing on-site air stripper was upgraded to provide additional blower capacity. A more frequent carbon change-out schedule was developed for the existing GAC columns and the existing air stripper off-gas activated carbon treatment system. The contaminated pond water was successfully treated in six weeks at a design flow rate of 80 gpm without any effluent parameter exceedences. This paper describes the treatability work performed at the site and the full-scale implementation of the selected treatment scheme.

#### POND WATER CHARACTERISTICS

The pond water characteristics and the discharge requirements are presented in Table 1. Several organics, including Volatile Organic Compounds (VOCs), Semi Volatile Organic Compounds (SVOCs), and metals parameters exceeded the discharge requirements and required additional treatment. The main VOCs of concern were vinyl chloride, 1,1-Dichloroethane (DCA), 1,1,2-Trichloroethane (TCA), and benzene. The SVOCs of concern were Bis(2-chloroethyl)ether (Bis) and phenanthrene. The main metals of concern were arsenic, chromium, and mercury. The total Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) concentrations in the pond water were 6,600 and 520 to 1,300 mg/L, respectively. Due to higher organics and metals concentrations present in Pond 1 water, the treatability investigations were conducted on Pond 1 water.

#### SCREENING TEST METHODS AND RESULTS

The treatability testing was divided into two phases. The first phase consisted of screening tests to determine the process technology and operating parameters. The second phase consisted of continuous flow bench-scale testing to determine design parameters and verify system performance.

The screening tests included batch metals precipitation treatment, batch chemical oxidation treatment, short term continuous-flow carbon adsorption, and batch air stripping. Titration curves were generated for the pond water samples to determine acid and caustic requirements. The results of the screening tests are described below.

#### **Metals Precipitation Batch Tests**

Batch tests were conducted to simulate metals precipitation treatment. One liter sample volumes were used in the jar tests. The pH of the water samples were raised to pH values of 7.0, 9.0, 10.5, and 12.0 s.u. using sodium hydroxide (caustic).

At pH values of 7.0 and above, floc formation and oil and water separation were observed. The mixed samples were analyzed for Total Suspended Solids (TSS), then allowed to settle for 30 minutes. The settled sludge volume was measured, and the supernatant was collected for metals analyses. Another set of jar tests was conducted using sodium sulfide in conjunction

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#### **Table 1. Pond Water Characteristics**

	Pond 1		nd 1	Pond 2	Discharge
Parameter	Units	Total	Dissolved	Total	Limit
TOC	mg/L	1,300	1,300	520	-
COD	mg/L	6,600	3500	-	-
BOD <sub>5</sub>	mg/L	880	520	-	-
TDS	mg/L	15,680		13,000	15,000
Oil & Grease	mg/L	350	-		-
Chloride	mg/L	6,400	-	· •	
Sulfate	mg/L	2,800	-		-
Hardness (total)	mg/L	4,400	-		-
Total Phenol	mg/L	5.9	-	-	
pH	s.u.	4.99	-	3	5 TO 10
TSS	mg/L	3,300	-	30	500
VSS	mg/L	2,700	-	-	-
Specific Conductance	µmhos/cm	19,620	-	-	-
Vinyl chloride	mg/L	7.8	-	0.14	0.2
1,2-Dichloroethane	mg/L	2.7	-	0.93	0.5
1,1,2-Trichloroethane	mg/L	64	-	0.56	1.9
Benzene	mg/L	ND	-	0.057	0.5
bis(2-Chlorethyl)ether	mg/L	0.29	-	0.68	0.25
Phenanthrene	mg/L	0.033	-	0.014	0.013
Arsenic	mg/L	0.01	0.012	< 0.004	0.01
Barium	mg/L	0.087	0.082	0.076	0.11
Cadmium	mg/L	0.0077	0.0094	<0.004	0.012
Chromium	mg/L	0.72	0.63	0.18	0.45
Lead	mg/L	2.8	1.7	0.054	4.3
Mercury	mg/L	0.037	<0.0002	<0.0002	0.001
Salenium	mg/L	<0.0020	<0.0020	<0.002	0.01
Silver	mg/L	<0.006	<0.006	<0.006	0.01

with caustic to precipitate metals. A sodium sulfide dose of 30 mg/L as sulfide was added to one liter samples at background pH and pH values of 7.0,9.0,10.5, and 12.0.

The test results showed that the discharge metals requirements were achieved by caustic precipitation at pH values of 7.0, 9.0, 10.5, and 12.0. The addition of sodium sulfide was not necessary to achieve the discharge limits. The supernatant iron concentration decreased at higher pH values. The supernatant iron concentration at pH 9.0 was 2 mg/L compared to the iron concentration of 110 mg/L at pH 7.0. To minimize the fouling of the subsequent air stripper treatment system, a metals removal pH of 9.0 was selected due to the lower effluent iron concentration.

#### **Chemical Oxidation Treatment Tests**

Ozone, ozone with hydrogen peroxide, and iron-catalyzed hydrogen peroxide oxidation technologies were tested. The chemical oxidation tests were performed on metals precipitation test effluent. Ozone was generated on-site using a portable PCl ozone generator. An average pond water TOC value of 1,250 mg/L was used for the chemical oxidation tests. Ozone to TOC ratios of 7.6:1 and 26.5:1 were tested. Hydrogen peroxide catalyzed ozone oxidation tests were performed at a peroxide dose of 1,250 mg/L and ozone to TOC ratios of 0.95,1.9, 3.8, and 9.5. Hydrogen peroxide oxidation tests were conducted at peroxide to TOC ratios of 0.48, 0.96, 1.92, 2.88, and 3.84. Iron catalyzed hydrogen peroxide tests were conducted at pH values of 9.0, 6.0, and 4.0, using a ferrous sulfate dosage of 100 mg/L as Fe and a peroxide dosage of 5,000 mg/L. The oxidized samples were analyzed for COD, TOC, pH, VOCs, and SVOCs. The results showed that chemical oxidation treatment by itself was unable to meet the discharge requirements at the dosages tested. No further testing with chemical oxidation was performed.

#### **Carbon Adsorption Short Term Continuous-Flow Test**

To conduct the carbon adsorption short term continuous-flow tests, a pond water sample was first pretreated for metals removal at a pH of 9.0 s.u. The metals treated sample was then divided into two portions. One portion of the sample was air stripped at an air to water ratio of 20:1 (v/v) and the other sample was not air stripped. Both samples were pumped via a peristaltic pump through a 0.5-inch diameter, 4-ft heigh, carbon column bed. After the passage of three bed volumes of water through the carbon, samples were collected and analyzed to determine organics removal efficiencies. Carbon adsorption treatment reduced the organics concentrations to less than the discharge requirements. Air stripping prior to carbon adsorption improved the removal of DCA, TCA, and Bis. The short term continuous-flow test results indicated that the existing on-site air stripping/carbon adsorption treatment preceded by metals removal was a suitable treatment scheme that could achieve the discharge requirements for the pond water.

#### **Batch Air Stripping Tests**

Batch air stripping tests were conducted to determine the air to water ratio required for VOCs and SVOCs removal from the pond water. The air stripping testing was conducted in a 5-gal glass container using bottled compressed air. Pond water was pretreated by metals precipitation prior to batch air stripping tests. A sample volume of 8-L was used. Air was bubbled at the bottom of the glass container using fine bubble air diffusers. An air flow rate of 10 scfh was used. Samples were collected over time to correspond to different air to water ratios. These samples were analyzed for COD, VOCs, and SVOCs. The results indicated no significant COD or TOC removal during air stripping. At an air to water ratio of 150, air stripping reduced the VOC concentrations to less than the method detection limits (MDL). Air stripping did not achieve any Bis removal.



FIGURE 1. Bench scale treatability flow schematic.

#### **Bench-Scale Treatability Testing Results**

To confirm the results of the screening tests and to develop design parameters, continuous-flow bench-scale treatability investigations were conducted. This second phase of testing included metals precipitation, air stripping, and carbon column adsorption treatment. A flow schematic of the continuous-flow treatment scheme is shown in Figure 1. The results of these treatability investigations are presented below.

#### **Metals Precipitation**

The continuous-flow metals precipitation system consisted of a pH adjustment chamber, a flocculation chamber, and an external clarifier. The pH in the pH adjustment chamber was maintained at a value of approximately 9.0 by adding 0.45 normal caustic into the chamber. The pH-adjusted water flowed by gravity to the flocculation chamber. An anionic polymer was added at a dosage of 10 mg/L to enhance flocculation. The flocculated water flowed by gravity to the clarifier. The clarifier underflow was pumped to a 5-gal waste solids collection container. The clarified effluent was collected in a 20-gal effluent container. The metals precipitation system effluent arsenic, barium, cadmium, chromium, lead, and silver concentrations were well below the discharge limits, throughout the testing period. Effluent selenium concentrations were below the method detection limit (MDL); however, in some instances, the MDLs were higher (0.34 mg/L) than the discharge limit of 0.010 mg/L. The majority of the time, effluent

mercury concentrations were below or equal to the discharge limit of 0.0009 mg/L. On two sample days, the effluent mercury concentrations were 0.0010 and 0.0050 mg/L, respectively. Average removals of 40, 27, 52, 93 and 66 percent were observed for arsenic, barium, chromium, lead, and mercury, respectively.

The waste solids quantities generated were monitored during the testing to evaluate solids handling during the full-scale treatment. Average TSS in the waste solids during the continuous-flow testing, was 29,275 mg/L. The quantity of waste solids generated was scaled-up to determine waste solids production at 80 gpm flow. The average waste solids production at 80 gpm was estimated to be 865 lbs/day on a dry weight basis. This was equivalent to a total waste solids production of approximately 22,500 lbs during the treatment of 3.0 mil gal of the pond water.

#### **Air Stripping Tests**

A continuous-flow air stripper consisting of a 1.5-inch diameter, 6ft tall glass column utilizing 5 mm size Raschig rings as a stripping medium, was used in the air stripping tests. The depth of the media bed was 3-ft. The air to water ratio was set at 45:1 to simulate the existing on-site air stripper (air flow of 475 scfm) air to water ratio at a flow of 80 gpm. No significant COD and TOC removals across the air stripper were observed. During the initial phase of the study, VOC

Run	Influe	nt			Effluent			Removal	
Time (days)	Chromium (mg/L)	Lead (mg/L)	Mercury (mg/L)	Chromium (mg/L)	Lead (mg/L)	Mercury (mg/L)	Chromium (%)	Lead (%)	Mercury (%)
1	0.74	3	0.029	0.25	0.081	0.0009	66.2	97.3	96.9
2	0.74	3	0.029	0.27	0.076	0.0004	63.5	97.5	98.6
5	0.62	0.96	0.002	0.24	0.046	0.001	61.3	95.2	50
6	0.62	0.96	0.002	0.004	0.046	0.005	99.4	95.2	-150
7	0.6	0.79	0.002	0.26	< 0.030	0.0007	56.7	96.2	65
8	0.53	0.46	0.001	0.26	< 0.030	< 0.0002	50.9	93.5	80
9	0.51	0.34	0.0008	0.24	< 0.030	0.0004	52.9	91.2	50
10	0.56	0.47	0.0007	0.31	< 0.030	< 0.0002	44.6	93.6	71.4
11	0.53	0.32	0.0006	0.31	< 0.030	0.0003	41.5	90.6	50
12	0.52	0.21	0.0002	0.3	<0.030	<0.0002	42.3	85.7	0
Averag	e 0.62	1.25	0.0083	0.229	0.046	0.0011	57.9	93.6	41.2
Limit	0.45	4.30	0.0009	0.45	4.30	0.0009			

#### Table 2. Pond Water Characteristics

Run	COD	COD (mg/L)		(mg/L)	DCA (Limit = 0.5 mg/L)		TCE (Limit = 1.9 mg/L)		Bis (Limit = 0.25 mg/L)		Phenanthrene (Limit = 0.0.13 mg/L)		Final Effluent
(hrs)	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	(mg/L)
0 3	4,800		1,040		<0.05		0.047		9.2		10.0		
8 24 30	3,040	400	1,200	80	<0.05	<0.05 <0.05	0.05	<0.05	14.0		2.5		<0.0002
37 48	3,200		1,084			<0.05 <0.05		<0.05 <0.05		<0.010 <0.010		0.010 0.010	
53 60		400 700		86 153		<0.05 <0.05		<0.05 <0.05		<0.010		0.010	
72 77	4,000	760 760	1,030	188 201	0.2	<0.05 <0.05	0.38	<0.05		<0.020		0.020	
83		800		209		<0.05		<0.05		< 0.013		0.013	
96 99 105	3,400	800 1,320 1,800	1,060	331 398 443	0.19	<0.05 <0.05 <0.05	0.31	<0.05 <0.05 <0.05	9.7	<0.012	5.6	0.012	0.0005
122	3,600	1,980	1,060	624	46	0.26	19	0.06	13.0	0.140	10.0	0.080	
134	3,520	2,820	1,060	913	52	3.9	19	0.60	11.0	0.980	10.0	0.100	0.0005

Table 3. Carbon Adsorption Test Results

removals to below the discharge limits were observed. However, a significant amount of the VOCs were removed in the continuous-flow metals precipitation step. DCA and TCA losses of 60 to 70 percent occurred in the metals precipitation system.

The average Bis removal during air stripping was 39 percent. Bis could not be stripped to levels below the discharge requirement in the study. The air stripper influent and effluent phenanthrene concentrations were always below the MDLs.

#### **Carbon Adsorption Treatment**

The air stripper effluent was treated by granular activated carbon adsorption. Two, 1-inch diameter, 6-ft tall carbon adsorption columns were operated in series in a down-flow mode. Each column contained a 4-ft bed of granular activated virgin carbon and represented one half of a 1 0-ft diameter full-scale dual module carbon adsorption column (10,000 lbs of carbon). The columns were operated in series, the first column being the lead column and the second as the polishing column. The influent was pumped to the top of the lead column using a peristaltic pump. Effluent samples from each column were monitored over time. A hydraulic loading rate of 1 gpm/sq-ft was used to simulate the full-scale system operation at 80 gpm flow through a full-scale skidmounted system. Grab effluent samples were collected for VOCs, SVOCs, TOC, and COD analyses. 24-hour effluent composite samples were collected for metals analyses.

The carbon adsorption analytical test results are presented in Table 3. Each column represented one half of a full-scale water treatment plant carbon adsorber (10,000 lbs of carbon). The COD and TOC breakthrough curves were generated. These data showed that the first full-scale carbon column (20,000 lbs of carbon) would be completely saturated after approximately 105 hours or 4.4 days of operation, with respect to COD and TOC.

Vinyl chloride, TCA, and benzene were not detected above the discharge requirements during the carbon column operation. The carbon column effluent DCA concentrations were below the discharge limit of 0.05 mg/L for 105 hours of operation. The influent DCA concentrations exceeded 0.2 mg/L at 122 hours of operation. These results indicated that a higher air to water ratio in the air stripper was needed to remove the DCA prior to the carbon columns to allow efficient and cost-effective use of the carbon. Further testing was required to determine how the treatment system would be designed and operated to cost-effectively achieve the required DCA removal.

The effluent Bis breakthrough curve data indicated that a full-scale dual column skid-mounted system (with 20,000 lbs of carbon/column) Bis breakthrough would occur in approximately 163 hours. The effluent phenanthrene concentrations were less than the MDL, although the MDLs were sometimes higher than the discharge requirement.

The final effluent metals concentrations were less than the discharge requirements throughout the testing period. The only metal of concern was mercury, since the other metals were reduced to less than the discharge limit in the metals precipitation step. The carbon adsorption treatment polished the effluent mercury concentrations. The highest effluent mercury concentration observed was 0.0005 mg/L as compared to the discharge limit of 0.0009 mg/L.

#### Effect Of Air Stripping On Carbon Adsorption

An additional carbon column test was operated to simulate carbon adsorption performance with relatively high VOCs concentrations exiting the air stripper, e.g., a worst-case scenario. This scenario simulated minimal VOCs and SVOCs removal during the pH adjustment and air stripping steps. The pH adjustment and flocculation steps were performed in a 5-gal container on a batch basis. Care was taken to minimize stiripper directly from the 5-gal container using a peristaltic pump. An air to water ratio of 45 (existing air stripper ratio at 80 gpm flow) was used in the air stripper. The column, representing 10,000 lbs of carbon, was operated for 58.5 hours. The column did not reach complete COD and TOC saturation after 58.5 hours of operation.

Effluent vinyl chloride concentrations were less than the discharge limit of 0.1 mg/L. The effluent DCA concentration exceeded the discharge limit of 0.5 mg/L after approximately 24 hours of operation. The effluent Bis concentration exceeded the discharge limit of 0.25 mg/L approximately after 42 hours of operation. The effluent phenanthrene concentrations were always less than the MDLs, however, the MDLs were higher than the discharge limit of 0.013



FIGURE 2. Flow schematic of pond water treatment system.

mg/L during this test. The effluent metals concentrations were less than the discharge limit throughout the testing period.

These results indicated that higher influent DCA concentrations will increase the carbon usage rates significantly, resulting in quicker change-outs and additional system down-time. An air to water ratio of 45 was not sufficient to strip the VOCs to the concentrations desired. A higher air to water ratio would be required to consistently strip the VOCs from the liquid stream and reduce the number of carbon changeouts. The Bis breakthrough characteristics were not impacted by the reduced air stripping in this test.

#### Air-To-Water Ratio Selection Test Results

Based on these results, it was concluded that the air-to-water ratio of 45 (v/v) in the existing full-scale stripper at a flow of 80 gpm was not adequate. A higher air to water ratio was needed to reduce the carbon usage and system down-time. Additional batch air-stripping tests were conducted to determine the required air to water ratio. The metals precipitation effluent was batch air stripped and samples were collected for VOC analyses at different air to water ratios.

These results indicated that an air to water ratio of 100 or more was required to reduce the influent VOCs concentrations to less than the discharge levels prior to carbon adsorption treatment. However, the influent DCA concentration in the test sample was 54 mg/L as compared to influent DCA concentrations of 250 to 300 mg/L observed in previous pond water samples. In order to provide adequate capacity to strip-off influent DCA concentrations of up to 500 mg/L to less than 0.1 mg/L, an air to water ratio of 200 was selected for design.

#### FULL-SCALE DESIGN CONSIDERATIONS

Based on the observed pond water characteristics and the results from the treatability study, it was concluded that the pond water could be treated to comply with the discharge requirements. The full-scale

treatment scheme would consist of a metals precipitation system, followed by an air stripper and carbon adsorption treatment system. The final effluent from the carbon treatment system would meet the discharge pretreatment requirements and no additional effluent polishing (e.g., chemical oxidation) would be required. Due to VOC losses in the metals precipitation system, the off-gas from the metals precipitation system would also require treatment. The existing air stripper could be used for pond water treatment. However, an air to water ratio of 200 would be required to consistently reduce the effluent VOCs to allow cost effective carbon treatment. The full-scale carbon adsorption system would consist of four carbon columns operated in series. The two lead columns would be changed out simultaneously after complete COD and TOC saturation occurred. This was expected to occur at approximately 210 hours or 8.8 days. This changeout would occur before Bis breakthrough in the final carbon column effluent.

#### FULL-SCALE DESIGN AND INSTALLATION

The full-scale treatment system consisted of metals precipitation and clarification, air stripping, and carbon adsorption treatment. The flow schematic of the full-scale water treatment system is shown in Figure 2. The metals precipitation system consisted of a pH adjustment tank equipped with a high-speed 0.5 hp mixer, a flocculation tank with a low-speed 1.0 hp flocculator mixer, and an effluent clarification system. Four 20,000 gallon capacity fraction tanks were located on-site. These tanks had previously been used for oil water separation. These tanks were cleaned and three of them were converted to settling tanks (metals precipitation clarification system). Wooden baffles were added in the settling tanks to prevent short circuiting of flow. Steel overflow doublel-weir collection boxes were constructed and installed for effluent collection. The fourth tank was converted to a solids thickener. The settled solids from the settling tank was pumped to the

20,000 gal solids thickener. The pH adjustment tank, the flocculation tank, and the mixers were new skid mounted units. Due to VOC losses in the metals precipitation system, the off-gas from the metals precipitation system was collected and treated by passing through 55 gal vapor phase carbon adsorber. The pond water was pumped to the rapid mix pH adjustment tank. Caustic was added in this tank to maintain a pH of 9.0 s.u. The pH adjusted water flowed by gravity to the flocculation tank. Polymer was added to the flocculation tank at a dose of 10 mg/L. The flocculation effluent flowed by gravity to the settling tanks.

The air stripper system included three 20,000 gal feed/storage tanks. Two of the tanks were used as the air stripper feed tanks and the third tank was converted to a surge tank. The clarified effluent flowed by gravity to the 20,000 gal air stripper feed tanks. The feed tank contents were pumped to the top of the air stripper. A new higher horsepower blower was added to the air stripper to provide an air to water ratio of 200 at an 80 gpm feed flow. The off-gas from the air stripper was treated in a 12,000 lb vapor phase activated carbon adsorber.

The effluent from the air stripper flowed to a 4,500 gal existing holding pond. The water from the holding pond was pumped to an existing dual module skid-mounted activated carbon adsorber. Another dual module adsorber was installed in series with the existing module to reduce the system downtime during carbon change-outs.

Three million gal of pond water was treated through the water treatment system during a period of 6 weeks. Compliance with discharge requirements was achieved during this period.

#### COST SAVINGS

The cost of the water treatment system described above, including new equipment, existing equipment modification, operations labor, and operation utilities, was approximately \$1,000,000. For a 3 million gallon volume, this is equivalent to \$0.33 per gallon of treated water. This cost includes 24-hour operator cover for the period of operation (approximately six weeks). The original estimate for off-site disposal of the pond water was approximately \$2,500,000 or \$0.83 per gallon. The net savings was approximately \$0.50 per gallon or a toal of \$1,500,000 for the treatment of 3.0 million gal of pond water.

#### SUMMARY

Wastewater treatment technologies were evaluated to pretreat approximately 3 million gallons of on-site contaminated pond water to meet POTW pretreatment requirements. A low cost water treatment scheme was developed, designed and installed and the contaminated water was successfully treated in a 16 week period. Bench-scale batch and continuous flow treatability testing were performed to evaluate advanced chemical oxidation, metals precipitation, air stripping, and granular activated carbon (GAC) adsorption treatment. A treatment scheme consisting of metals and O&CG removal, air stripping, and GAC adsorption polishing was designed and installed. Upgrade of the existing treatment system was performed to minimize the cost of new equipment and installation time. The contaminated pond water was successfully treated in six weeks at a design flow rate of 80 gpm without any effluent parameter exceedences. The rapid design, installation, and operation of the treatment system resulted in tremendous cost savings and the facility was able to meet the pond closure schedule.
# *In Situ* Biological Treatment of TCE-Impacted Soil and Groundwater: Demonstration Results

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An in situ biological treatment technique designed to destroy trichloroethylene (TCE) was demonstrated at field scale at a manufacturing facility in the Midwest. Air and methane were injected into the contaminated groundwater through a vertical sparge well, while air was extracted from the vadose zone though a well screened in the unsaturated zone. A mobile demonstration test trailer housing air injection compressor, soil venting blower, and methane injection equipment was used to allow rapid equipment deployment, setup, and demobilization. Air and methane act to stimulate indigenous microorganisms to degrade TCE and dichloroethylene (DCE) via aerobic cometabolism. Toxic degradation products, such as vinyl chloride, are not generated by methanotrophic cometabolism.

The demonstration was conducted over a three-month time period, with groundwater and soil gas monitored weekly for several chemical and microbiological parameters. The test successfully stimulated the methanotroph population to increase over one order of magnitude and soil gas carbon dioxide (a by-product of biodegradation) concentrations to increase when methane was injected into the aquifer. In addition, groundwater volatile organic compounds were reduced by 60 to 80 percent in the groundwater monitoring wells that were sampled.

#### INTRODUCTION

An in-field test was conducted to demonstrate the feasibility of using Chlorinated Treatment by Methane Injection (CTMI) to remediate groundwater impacted with trichloroethylene (TCE) and related chlorinated organics. CTMI is an aerobic cometabolic in situ bioremediation technology that works by stimulating indigenous microorganisms to degrade chlorinated solvents as they metabolize methane, their primary substrate. Success of the demonstration test would be indicated by an increase in methanotrophic organism population that concurred with a decrease in groundwater contaminants. Success hinged on the ability to deliver air and methane to the impacted subsurface area.

#### Site History

The site was located at a stainless-steel products fabricating facility in northeast Missouri. The facility has been and continues to operate as a stainless-steel fabricator. Groundwater and soil were impacted with a chlorinated solvent, TCE, and degradation products dichloroethylene (DCE) and vinyl chloride (VC). Toxic degradation products such as DCE and VC are typically produced by intrinsic anaerobic biodegradation. Concentration of groundwater contaminants ranged up to 30,000 micrograms per liter ( $\mu$ g/L) TCE, 5,000  $\mu$ g/L DCE, and 25  $\mu$ g/L VC. Groundwater impact extended to 40 feet (12.2 meters) below ground surface (BGS) in some areas.

The source of contamination was unknown although several potential sources existed including subsurface vapor degreasers, TCE storage tanks, and fenceline spraying of waste solvent for weed control. Although the facility is still in operation, ongoing releases were believed to have ceased.

Site soils were alluvial in nature, consisting of interbedded clay, sands, silts, and gravels. Groundwater elevation fluctuated between 15 feet and 20 feet (4.6 and 6.1 meters) BGS, influenced by the water level of the creek adjacent to the west edge of the site and the Missouri River located one-half mile (0.8 km) north and northeast of the site

A groundwater recovery and air stripping system had been operating for 5 years previous; however, decreases in groundwater contaminant concentrations had been small and had appeared to reach the point of diminishing returns. The client wanted to increase the cleanup rate and minimize the life cycle cost of remediation.

#### TECHNOLOGY DESCRIPTION

CTMI is an *in situ* bioremediation technique developed at US Department of Energy's Savannah River Site in 1992 and later patented [3].



FIGURE 1. MMO Oxidation of TCE.

The technology is based on stimulating indigenous microorganisms, called methanotrophs, to degrade chlorinated solvents and other typically recalcitrant compounds by introducing oxygen and methane into their environment. Methanotrophs degrade TCE fortuitously (without any benefit to the methanotroph) as methane is metabolized. As methanotrophs metabolize methane, they produce an enzyme, methanemonooxygenase (MMO). MMO is the primary enzyme causing degradation of TCE. MMO is a very powerful, non-specific oxidizer that is capable of oxidizing a wide variety of typically recalcitrant compounds. MMO inserts an oxygen atom into the ethylene molecule to create an epoxide, as shown in Figure 1. The epoxide is unstable and spontaneously breaks down into small compounds that are easily and quickly degraded by heterotrophic microorganisms into carbon dioxide and chloride salts [1]. Although methanotrophs are the focus of the technology, a heterogeneous population of microbes is needed for complete mineralization of TCE to carbon dioxide, water, and chloride salts. Toxic degradation products such as DCE and VC are not formed by methanotrophic biodegradation.

Methane, air, and vapor-phase nutrients (if needed) are injected into the subsurface through air injection wells screened just below the impacted groundwater. As these essential components are introduced to the methanotrophs, their populations increase, and methane and chlorinated solvents are destroyed. Soil venting wells, screened in the vadose zone and connected to soil venting blowers, are designed to contain injected gases and assist in drawing the vapors up through the impacted groundwater and soil.

CTMI is often used in conjunction with air sparging/soil venting (AS/SV) operations. Air sparging and soil venting are mass-transfer-based treatment technologies where contaminants are transferred from dis-



FIGURE 2. Schematic of CTMI treatment.

solved or sorbed state to vapor state, and brought to the surface for treatment (See Figure 2). At high concentrations, an AS/SV operation is very effective; however, its effectiveness decreases as concentrations decrease. CTMI is effective at lower concentrations; at about 1-10 mg/L CTMI treatment will become more economical than air sparging and soil venting.

State agencies that have been contacted regarding permitting requirements for potential CTMI demonstrations have been receptive to the technology. The primary concern is monitoring compounds that are introduced into the subsurface. CTMI is currently listed on the Texas Natural Resource Conservation Commission's List of Designated Innovative Technologies as a bioremediation process for chlorinated organics.

#### **CTMI DEMONSTRATION**

The demonstration was undertaken to decide if TCE at the site could be destroyed using the CTMI technology.

Why run a CTMI demonstration Test?

- · Be sure that methanotrophs are present and can be stimulated.
- Assess reduction of VOCs in groundwater.

#### **Goals of CTMI Demonstration**

Several criteria are important to the successful implementation of CTMI:

- Criteria to Evaluate During Demonstration:
- 1. Ability to move air and nutrients through the subsurface.
- 2. Reduction of groundwater VOCs.
- 3. Ability to stimulate the growth of methanotrophs.

Tests to evaluate physical design parameters such as air injection and soil venting radius of influence are employed along with the bioremediation evaluation. The demonstration is targeted at evaluating whether methanotrophs can be stimulated and whether additional nutrients are needed to allow a population increase.

#### Challenges of field testing

The effectiveness of *in situ* bioremediation of TCE is best demonstrated and evaluated in the field because simulation of the natural microbial ecosystem either by computer modeling or bench-scale tests is not generally representative or transferable to full-scale design parameters. However, field demonstrations present several challenges to data gathering and evaluation.

1. The goals of field testing are different from research work. The client's question is: "Can we clean up the site?" Research work aimed at understanding detailed elements of a process does not necessarily change the overall effect of a process. Field setup and information gathering must recognize the client's information needs first.

2. Field demonstrations have time and budget constraints that limit the information collected during the test. Conclusions must often be drawn from less than optimal data sets.

3. Field demonstrations lack an experimental control. An experimental control would greatly increase the ability to accurately identify and quantify the VOC reduction mechanism at work. However, clients are not typically willing to pay for the additional equipment, labor, and information gathering costs associated with setting up an experimental control.

4. Direct measurements for biodegradation are often not attainable. Indirect measurements, such as using carbon dioxide (CO<sub>2</sub>) concentration and chloride concentration as indications of TCE mineralization, can be influenced by physical characteristics that are extraneous to the biological system.

#### Table 1. Background Levels for Test Parameters

Parameter	Concentration	Comments
Total groundwater VOC	46.3-40, 100 ppb	some TCE and DCE included
Dissolved oxygen	0.8-2.1 mg/L	low DO in wells with high methane
Chloride	4.75-23.7 mg/L	high background concentrations may interfere with tracking during test
pH	7.0-7.5	neutral
Methane	2.1-1, 898 mg/L	values high, indicating anaerobic activity
Total Heterotrophic Plate Count	6,900-8,100 cells/ml	one strain identified as TCE-degrading
Methanotrophic MPN		lab unable to conduct test
Total Organic Carbon	0.3 - 2.2 mg/L	low
Total Nitrogen	0.14 - 3.1 mg/L	may become limiting
Total Phosphorus	0.24 - 14.2 mg/L	may become limiting in some wells

 Methods for identifying methanotrophs are not yet common or codified.
 Enumerating methanotrophs is still considered state-of-the-art, and not all laboratories are capable of producing reliable analysis.

6. Finally, the study area cannot be isolated in the field. Influx of ground-water, groundwater level fluctuations, and migration of contaminants must be considered when conducting the demonstration study. Mass balance calculations on the contaminant are not possible to any degree of accuracy.

An understanding of the limitations of field testing does not invalidate the results, but allows us to interpret them in a sound engineering manner. Caution must be used in not overstating the conclusions reached as a result of field testing.

#### **Pre-Demonstration Tasks**

Several tasks were undertaken prior to performance of the demonstration study. These are briefly discussed below:

#### System Permitting

The Missouri Department of Natural Resources (MDNR) required an Underground Injection Control (UIC) permit to allow injection of methane into the groundwater. The MDNR requires UIC permits when sub-



FIGURE 3. Site map.

stances other than air or water are to be injected into the state's groundwater. Conditions of the permit required collection of methane samples in groundwater both before and after the demonstration to document return to background levels after the test. The soil venting vapor discharge received a permit waiver because anticipated discharges were below MDNR's *de minimus* quantity. The "biological" portion of the demonstration required no special permitting.

#### Design

The demonstration study system was designed to evaluate the area closest to high groundwater VOC concentrations, and existing monitoring wells (deep and shallow) were used for the study. Figure 3 illustrates the demonstration test layout.

One 2-inch (5.1 cm) diameter air injection well (SP-1) screened from 39 to 41.5 feet (11.9 to 12.6 meters) BGS and one 4-inch (10.2 cm) diameter soil venting well (VW-1) screened from 10 to 20 feet (3 to 6 meters) BGS were installed for the demonstration test. Existing groundwater monitoring wells (MW-1, MW-5, MS-1, MS-2) were used to collect data for evaluation.

A demonstration test trailer was brought to the site fully equipped with a piston-type air injection compressor, regenerative soil venting blower, and methane injection apparatus. Injected air was filtered, methane was injected into the header, and the flow metered. The flow of vapors from the soil venting blower was metered through a rotameter flow meter before discharge to the atmosphere.

Research-grade methane (99-percent purity) without odorant was supplied in four 350-cubic-foot (10 cubic meter) cylinders. The cylinders were connected, via manifold, to a two-stage regulator and rotameter flow meter. Methane gas was injected into the air injection header through a methane control solenoid. A reed switch on the flow meter closed the methane control solenoid to stop the flow of methane when the flow of air stopped.

#### Sampling

In order to assess the applicability of CTMI, background information was gathered prior to commencement of the demonstration. The background information was used initially to evaluate the feasibility and also to evaluate performance throughout the testing. Since testing can be costly and time consuming, bioremediation performance was assessed using indirect parameters, based on knowledge of metabolic and reaction processes. Prior to startup of the air injection and soil venting tests, baseline data were collected. Table 1 lists the parameters determined.

The background levels in the study area indicate that CTMI could be successful. The VOC levels, while high in one well, were below levels that are considered toxic for methanotrophs. The relatively high concentrations of methane, low concentrations of dissolved oxygen, and presence of DCE and VC indicated that anaerobic microbial biodegradation was likely occurring before the demonstration test began. Chloride concentration in the groundwater is typically used to indicate the destruction of chlorinated compounds, since chlorine is released as the compounds break down. The relatively high background chloride concentration limited the use of chlorides as an indicator.

A most probable number (MPN) for methanotrophs was requested, but the contract laboratory was unable to perform the analyses as promised, and a baseline for methanotrophs was not obtained for the demonstration.

The low concentration of total organic carbon indicates that there would be little competition for, or interference with, MMO oxidizing TCE.

Nitrogen and phosphorus concentrations were low in some wells. Guidelines for adding nitrogen and phosphorus with the methane indicate that C:N:P ratios be approximately 500:10:1. Based on the total VOCs in the groundwater (up to 40,000 ppb), background levels of nitrogen should be 0.8 mg/L or greater, and phosphorus should be at or above 0.08 mg/L. More nitrogen and phosphorus would be needed because of the addition of methane as a carbon source. The relatively low concentrations of nitrogen and phosphorus in some wells may become limiting in a full-scale project. However, for a demonstration study, we felt that there was probably sufficient nitrogen and phosphorus. Monitoring these parameters during the study gave the insight needed for full-scale design.

#### Phase I: Air Injection and Soil Venting Tests

Goals:

- 1. Define air injection and soil venting radii of influence.
- 2. Evaluate vacuum and injection pressures and flow rates.

The applicability of CTMI as a remedial measure at a site is largely dependent on the ability to transfer vapor-phase nutrients to the subsurface. Thus, the air permeability of the vadose zone, permeability and saturated thickness of the aquifer, heterogeneity of the geologic formations, and volatility of the contaminants must be evaluated, and design parameters developed from the field study.

Air injection and soil venting tests were conducted to evaluate the application of and design of the air injection and venting components of CTMI. Design parameters were developed by gathering information about pressure changes, air flow, and VOC mass transfer induced by applying a vacuums to the vadose zone, and injecting air into the saturated zone of the site.

The soil venting test was conducted over three days by applying a vacuum to the vent well, and measuring pressure change in piezometers and monitoring wells. The venting test indicated that the vapor-phase permeability of the formation near the soil venting well is low. Venting radius of influence was measured between 15 to 20 feet (4.6 to 6.1 meters) from VW-1 when a vacuum of 40 inches of water (in.  $H_2O$ ) (75 mm Hg) was applied. The maximum venting flow rate attained at this vacuum was 18 cubic feet per minute (cfm) (0.5 cubic meters per minute [m<sup>3</sup>/min]). The predominance of clay in the vadose zone in the vicinity of VW-1 apparently inhibits the flow of air, reducing the efficiency of soil venting at that location.

Vapors generated during the vent tests were collected and analyzed

for VOCs. Maximum total VOC concentration during the soil venting test was 21 parts per billion by volume (ppbv).

Air injection testing indicated that between 5 and 8 cfm (0. 15 and 0.23 m3/min) of air could be delivered to the subsurface (into the groundwater) under 20 pounds per square inch (psi) (41 mm Hg) pressure. Results also indicated an effective air injection radius of influence of approximately 30 feet (9 meters) based on pressures and dissolved oxygen readings at several points located at known distances from SP-I. Influences from air injection were also observed at monitoring well MW-5, located approximately 350 feet (107 meters) from SP-1, during later stages of the demonstration test. These influences are believed to be caused by the collection of sparged air underneath a clay lens located below the groundwater table. As this air collected underneath the clay lens, it apparently migrated up-dip to the first available point of escape to the surface. The construction of MW-5, screened in a relatively high-permeability sand lens, apparently provided a pathway of least resistance for the collected air to reach the surface. This anomaly in the air flow patterns influenced the parameters monitored at wells in the demonstration study.

Soil vapor VOC concentrations measured at the monitoring wells and at the soil venting well remained very low even after air injection was initiated, except at MW-5, where concentrations as high as 122 parts per million by volume (ppmv) were recorded.

#### Phase II: CTMI Test

CTMI Test Measure of Success:

- Increase in methanotrophic populations
- Increase in CO2 in soil gas
- Decrease in groundwater VOCs

The CTMI test began on November 2, 1994, and continued through February 17, 1995. Air was injected and vented throughout the CTMI test period. Methane injection was conducted in four separate campaigns under different operating conditions.

The air injection rate was varied between 1.5 cfm and 5 cfm (0.04 and 0.14 m<sup>3</sup>/min) during the CTMI test, with the soil venting air flow rate set at 3 to 16 cfm (0.08 to 0.15 m<sup>3</sup>/min) to minimize the amount of contaminant volatilization. Methane concentrations were varied between 1 percent and 1.8 percent v/v of the injected air flow. The highest concentration was applied during the first campaign, and after groundwater methane concentrations were observed, a lower concentration was used. No additional nutrients were injected with the methane and air.

Several parameters, listed in Table 2 were monitored to evaluate the success of CTMI. Three tests were used during Methane Injection Campaign 4 to enumerate and identify methanotrophs in the groundwater: MPN-Methanotrophs, total viable biomass measured by Phospholipid Fatty Acids (PLFA), and gene probe analysis. The MPN test was adapted to be specific

#### Table 2. Analysis During CTMI

Groundwater	Soil Gas	
VOC	CO <sub>2</sub>	
MPN-Methanotrophs	Hydrocarbons	
PLFA	Methane	
Gene Probe		
THPC		
Methane		
Chloride		
DO		



FIGURE 4. Groundwater dissolved oxygen. Monitoring wells MW-1 MW-5, MS-2. Full project.

to methanotrophs. The MPN-methanotroph test determined the population of methanotrophs in cells per volume of water. Analysis of total viable biomass provided an indication of the population of viable (living) or potentially viable microorganisms, and was used to assess the relative metabolic status of the microbial community. A microbial community that is increasing will have a significant number of younger (viable) cells, and a lower total viable biomass indicates dying/dead cells of a microbial community in decline. A gene probe was used to identify the gene-encoded MMO enzyme that is produced by, and is specific to, methanotrophs.

In the initial phases of the CTMI study, Total Heterotrophic Plate Counts (THPC) were conducted in an attempt to establish a correlation between THPC and MPN-methanotroph results. (THPC are easier and less expensive to conduct.)

Carbon dioxide (CO<sub>2</sub>) was measured in the soil gas as an indication

of metabolic activity.  $CO_2$  was measured using an infrared  $CO_2$  meter. Dissolved oxygen (DO) in groundwater was measured using a field DO probe. Soil-gas hydrocarbons were not measured directly in the field. A photoionization detector (PID), typically used for air monitoring, was used to measure relative presence of VOCs in the headspace of the monitoring wells. The wells were kept covered between sampling events, and the PID was placed in line with an air pump that vented the headspace. It should be noted that the PID does not measure methane, nor does it directly quantify the VOCs. The most prudent use of the PID information was as a relative indicator of the increase or decrease in volatilized VOCs.

#### DISCUSSION OF DEMONSTRATION RESULTS

Three criteria that were to be evaluated were: the ability to move nutnents through the subsurface, reduction of groundwater VOCs, and the abil-



FIGURE 5. Groundwater dissolved methane. Monitoring wells MW-1, MW-5, MS-2. Full project.



FIGURE 6. Groundwater VOCs. Monitoring wells MW-5, MS-2. Full project.

ity to conclude that the destruction of VOCs was due to biological activity. A discussion of the results as they relate to the demonstration is given below. Because Methane Injection Campaign 4 was sampled and actually analyzed extensively for microbial parameters, it is the focus of this discussion.

#### 1. Ability to move air and nutrients through the subsurface.

As shown in Figures 4 and 5 we were able to get air and methane through the subsurface formations. The heterogeneity presented challenges, with clay lenses in the vadose zone impeding flow and a sand lens acting as a conduit for air flow. With reduced air injection flow rate and pressure, the lateral migration of air and methane was controlled in the sand lens.

The mass balance elements for dissolved oxygen include 1) increase due to injected air, 2) decrease due to microbial use, 3) decrease due to influx of low DO groundwater, and 4) other abiotic oxygen uses. DO concentrations in all wells monitored generally remained greater than 1 mg/L which is sufficient for the aerobic methanotrophs to live. The DO content of the groundwater in MW-1, a well close to the air injection well, decreased slightly during initial air injection, then increased steadily from 1.5 mg/L to almost 6 mg/L. The DO reading in MS-2,



FIGURE 7. Groundwater level. Monitoring wells MW-1, MW-5, MS-2. Full project.



FIGURE 8. Groundwater methanotroph population. Monitoring wells MW-1, MW-5, MS-2, MS-1. Methane campaign 4.

close to the injection well, but screened in the shallow groundwater, increased most dramatically during days 14 to 64 (from 2.4 to 4.9 mg/L), but tapered off during the later days of the CTMI testing. The airflow during the later days was also lower than the earlier stages of the CTMI test. Increased methanotroph activity could be responsible for the lower dissolved oxygen levels. The DO concentrations in MW-5 were erratic, which is not unusual, given the distance (350 feet or 107 meters) between the air injection point and the well. The DO concentrations in MS-1 remained low, and MS-1 was selected for observation as a background well and appeared to be only minimally effected by the injected air.

The mass balance elements for methane are similar to those for oxygen. Methane concentrations in groundwater increased during the methane injection campaigns. The concentrations were highest during the first methane injection campaign, when the rate of application was approximately 1.2 percent. The concentrations were lower for subsequent campaigns, even with an increase in the application rate. Increased methanotrophic activity could be responsible for the lower methane concentrations.



FIGURE 9. Microbe activity indicators. Monitoring well MW-1. Methane campaign 4.



FIGURE 10. Microbe activity indicators. Monitoring well MW-5. Methane campaign 4.

An influx of groundwater with a low methane concentration and groundwater level fluctuations could also influence the methane concentration.

Nitrogen and phosphorus were analyzed once before beginning and once after the demonstration test was complete. Although we decided that initial nitrogen and phosphorus levels were sufficient to carry out the demonstration, by the end of Methane Injection Campaign 4 concentrations were probably limiting the response of the methanotrophs to the methane injection.

#### 2. Reduction of groundwater VOCs

Groundwater VOCs decreased in the monitoring wells considered for this

demonstration. Demonstration test activities caused TCE in groundwater to drop by 60 to 80 percent of the initial groundwater VOC concentrations (Figure 6).

Groundwater fluctuated over a four-foot (1. 2-meter) interval during the course of the demonstration test, as shown in Figure 7. Periods of high groundwater level generally coincided with higher groundwater VOC concentrations as VOCs hung up in the capillary fringe dissolved into the groundwater as it rose. The groundwater level was rising during this campaign, and may have influenced the spike in concentration at the beginning at day 100.

Two mechanisms have been identified in the reduction of VOCs in the groundwater: volatilization and biodegradation. If volatilization is a significant



FIGURE 11. Groundwater methanotroph population and VOCs. Monitoring well MW-1. Methane campaign 4.



FIGURE 12. Groundwater methanotroph population and VOCs. Monitoring well MW-5. Methane campaign 4.

mechanism, then the headspace of the monitoring wells would show a relatively high concentration of VOCs, and these would remain constant throughout the demonstration because air was injected into the groundwater for the entire demonstration. In addition, we would not see correlation between methanotroph activity and reduction of VOCs in the groundwater.

Soil vapor VOC concentrations remained low even after air injection was initiated, except at MW-S, where relatively high concentrations were found. This is likely the result of some mass transfer of VOCs through the sand lens.

#### 3. Measures of Biological Destruction of Contaminants

Three primary parameters were used to evaluate the destruction of contaminants via biological mechanisms. Increase in methanotroph population, concurrent decrease in groundwater VOC concentration, and increase in carbon dioxide all point to a biological destruction



FIGURE 13. Vapor-phase carbon dioxide trends. Vent and monitoring wells MW-1, MW-5. Full project.

mechanism. These three parameters are discussed below.

#### Ability to stimulate tlie growth of methanotrophs

Measurements of methanotroph population by MPN-methanotrophs, PLFA, and gene probes were conducted during Methane Injection Campaign 4. The changes in methanotroph population in wells monitored are shown in Figure 8, and additional activity indicators shown in Figure 9 and 10.

All monitoring wells showed an increase in methanotroph population after methane was injected during Campaign 4. Monitoring wells MW-I and MW-5 contained the highest biomass of methanotrophic microorganisms among the wells tested. The population peaked at Day 110, five days after Methane Injection Campaign 4 began. Methanotrophic populations in MS-2 peaked on Day 113, eight days after methane injection began. Methanotroph populations showed a decrease before the methane injection was terminated. Monitoring well MS-1, chosen as a background well and not influenced by the injected air, had initial methanotroph populations that were much lower than the other wells and showed no response to methane injection.

The microbial communities cultured by the laboratory showed a pink tint characteristic of methanotrophs and also tested positive for the MMO gene specific to methanotrophs. Trends in total viable biomass, extrapolated from the PLFA data, peaked on day 110 (three days before the MPNmethanotroph peaked). PLFA analysis of MS-2 indicated that environmental stress due to starvation was initially high before Campaign 4 began and decreased when methane injection was begun.

#### Decrease in groundwater VOC concentration concurrent with increase in methanotrophic population

Groundwater VOC concentrations during Methane Injection Campaign 4 fell slightly during the nine days methane was injected, then dropped off precipitously after methane injection was stopped. These trends are shown in Figures 11 and 12. The decrease in VOC concentration in the groundwater lagged a significant increase in the methanotroph population during Methane Injection Campaign 4.

#### Increase in CO<sub>2</sub>

If methanotrophs are present and active we should observe an increase in the concentration of  $CO_2$  in the water and soil gas as a result of mineralization of TCE. Carbon dioxide concentrations are shown in Figure 13. Carbon dioxide is an extremely volatile compound, and its concentration in soil gas will be influenced by the concentration in groundwater and in airflow through the groundwater that will transfer most of the  $CO_2$  to soil gas. Only soil gas  $CO_2$  was monitored, and the correlation between  $CO_2$  in soil gas and biological activity would be expected to be somewhat muted.

However, like the soil gas PID readings, soil gas  $CO_2$  readings can be used to judge relative production of  $CO_2$  by microorganisms in both the saturated and vadose zones. Concentrations of  $CO_2$  in monitoring wells MS- 2 and MW-5 gradually increased after air injection was initiated at the beginning of the study. Concentrations of  $CO_2$  were low (approximately one percent) before Methane Injection Campaign 4 began. Carbon dioxide concentrations increased in MW-5 when methane injection was initiated and dropped off when methane injection was terminated. Carbon dioxide concentrations in MS-2 and MW-1 remained low throughout Methane Injection Campaign 4.

#### CONCLUSIONS

CTMI Test Measure of Success

- · increase in methanotropic populations
- increase in CO<sub>2</sub> in vent gases
- decrease in groundwater VOCs

CTMI can be used to successfully remediate the VOCs that contaminate groundwater and soil at this site. Methanotrophic bacteria are naturally occurring in groundwater at the site and can be stimulated through the injection of air and methane into the subsurface. Methanotroph population increased over one order of magnitude in response to methane injection in Methane Injection Campaign 4.

The  $CO_2$  in the soil gas increased, after methane injection was begun. The relatively low  $CO_2$  levels toward the end of the demonstration study, and the decrease in phosphorous concentrations and relatively low nitrogen concentrations indicate that provisions to inject vapor-phase nitrogen and phosphorus will need to be incorporated into the frill-scale design of a CTMI system.

Groundwater VOCs were reduced by 60 to 80 percent in Monitoring Wells MW-1 MW-5, and MS-1. The overall trend of VOCs was downward, although some fluctuation was observed, possibly because of groundwater fluctuation.

The heterogeneity and stratification of site geology requires careful design of the full-scale system to ensure that oxygen, methane, and nutnents permeate into all impacted zones.

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# NO<sub>X</sub> PEMS Experience on Operating Ethylene Furnaces

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The Phillips 66 Sweeney Refinery and Petrochemical Complex is a highly integrated complex consisting frefining, chemicals, and ethylene units. The Complex received a Texas Natural Resource Conservation Commission (TNRCC) Flexible Permit to install predictive emissions monitors (PEMS) at eight furnaces of Ethylene Unit 22.

Unit 22 produces approximately 1.8 million pounds per day of ethylene. Hydrogen in the fuel gas fluctuates between 20% and 80% depending on economics and the operational status of upstream and downstream units. Maintaining consistent fuel gas bydrogen levels and unit upsets made it difficult to train the models. The PEMS is certified and has been in full operation since March 1996. The difficultes and successes of the PEMS certification process is discussed in this paper.

#### INTRODUCTION

The Phillips 66 Sweeny Refinery and Petrochemical Complex is a highly integrated complex consisting of refining, chemicals, and ethylene units. The Sweeny Complex is the world's largest single site of ethylene production. This ethylene production is accomplished with several operating units, each with similar ethylene cracking furnaces.

The Complex opted to apply for a Texas Natural Resource Conservation Commission (TNRCC) Flexible Permit in order to gain operational flexibility. The permit required Reasonably Available Control Technology (RACT) controls on all furnaces. The permit also specified that continuous emissions monitors (CEMS) or predictive emissions monitors (PEMS) be installed on the furnaces of two "grandfathered" units by set dates.

Given that our estimated capital cost for PEMS installation and maintenance was roughly half that estimated for CEMS, we were eager to try the PEMS technology. A decision was made to install NO<sub>x</sub> and O<sub>2</sub> PEMS at eight furnaces at Ethylene Unit 22. Since NOx, CO and O<sub>2</sub> CEMS were in operation at another existing ethylene unit at this facility, this allowed us a unique opportunity to evaluate the advantages of each technology.

This paper covers our experience with PEMS installation and operation at this facility only. We continue to be "on the learning curve" with the PEMS technology since our PEMS have been in full operation only since March 1996. Any observations are made as a result of this experience. Since Sweeny Complex is made up of many highly integrated and interdependent process units, the ethylene units probably experience more variability in operating conditions than other facilities.

#### UNIT CONSIDERATIONS

Unit 22 is an ethylene unit which produces approximately 1.8 million pounds per day of ethylene. The unit's eight gas-fired furnaces were designed by Kinetics Technology, Incorporated and are rated at 130 MMBTU/hr (higher heating value). Each furnace has 24 floormounted John Zink burners and operate at temperatures in excess of 1500° F.

Ethane feed is supplied from NGL fractionation units. Uncracked ethane is recycled as feed to the furnaces. The NGL units also provide the primary source of furnace fuel gas-propane and isobutane. Unit 22 can also recycle its own tail gas, and tail gas from other ethylene units. Unit 26.2 takes in hydrogen and prepares it for use in crude desulphurization. Hydrogen in the fuel gas fluctuates between 20% and 80% depending upon economics and the operational status of upstream and downstream units.

PEMS were established on the eight Unit 22 ethylene furnaces beginning in September 1995 per the requirements of the Flexible Permit. The PEMS models, fully tested and proven, have been in operation since March of 1996.  $NO_x$  and  $O_2$  prediction accuracy has improved at each relative accuracy (RATA) test. The most recent RATA test was more than five percent accurate, which qualifies us for an extension to one year of our next required RATA test. A summary of RATA testing results is located in the Appendix 1.

#### PERMIT CONSIDERATIONS

At the time the permit conditions were negotiated with the state, the NOx RACT rule (TNRCC Regulation VII) was subject to an administrative stay pending the outcome of the COAST (Coastal Zone Oxidant Assessment Study of Southeast Texas) study, air dispersion modeling and analysis to determine whether NOx reductions in the Houston-Galveston nonattainment area would result in lower ozone concentrations. Given TNRCC's acceptance of PEMS in lieu of CEMS for compliance with the NOx RACT,

the state readily accepted our proposal to install NOx PEMS at Unit 22 as part of the flexible permitting process [1].

The permit requires annual EPA reference method stack tests in addition to the relative accuracy testing and statistical test analyses to verify compliance with RACT levels represented in the permit application and hourly and annual emissions caps specified in the permit. Only initial EPA reference method stack tests are required for ethylene units equipped with CEMS, and quarterly cylinder gas audits are acceptable in lieu of RATAs.

The permit also required the development of a quality assurance plan/manual that ensures continuous and reliable performance of the PEMS. It required the establishment of a frequency for calibrating each sensor whose readout serves as an input to the model.

The facility flexible permit special conditions require that a petition to the TNRCC Executive Director be submitted for approval to install a PEMS or to replace a CEMS with a PEMS. The petition must include results of tests conducted beforehand to demonstrate equivalent accuracy and precision of PEMS to that of hardware CEMS. For a PEMS installed to replace a CEMS, both systems must remain in place at least one operating quarter collecting valid information before the CEMS is removed.

#### SENSORS CHOSEN FOR THE PEMS MODEL

The PEMS vendor requested a list of all sensors available. They picked a long list of sensors most likely to influence  $NO_x$  formation and we set up a program to monitor those sensors. Then the vendor picked the sensors with the highest established correlation to  $NO_x$  formation, and assigned an importance ranking to each sensor for each furnace. Together we chose the sensors that would be the inputs to the model. A detailed breakdown of the sensors chosen for two representative furnaces appear in Appendix 2.

The PEMS sensor validation models were developed for each furnace at high and low hydrogen in fuel situations. The building of the models took considerably longer than the estimated five days per scenario due primarily to problems with maintaining consistent fuel gas hydrogen levels and unit upsets.

#### PEMS COMPUTER AND DATA STORAGE/FORMAT

The PEMS models were implemented on a IBM, 90 MHz Pentium computer with 32 MB system memory, one 524 MB system hard disk, one 3 GB data hard disk and one 150 MB removable disk drive. The operating system is Windows for Workgroups 3.11. Two PEMS models predict NO<sub>x</sub> and O<sub>2</sub> for three furnaces each, and one model predicts NO<sub>x</sub> and O<sub>2</sub> for two furnaces. The models are supported by Pavilion Run Time Products \*. The database and graphical user interface is Wonderware InTouch 5 \*\*.

Initially, the PEMS models were slightly unstable, tending to lock up or get general application errors. The contractor provided several successful "bug fixes" to correct this. The most significant fix was a program that detects if a model is developing a problem and shuts the questionable model down. Also, every three minutes a "watchdog" program checks the models, and automatically restarts them if they are down. When this restart occurs a message is written to a log file which provides a means for monitoring restarts (or general health of the system). The restarts are transparent to the user and do not occur often. The PEMS models store process input, predicted output and alarm data in log files. The log files can be converted to spreadsheet for evaluating time and date stamped data. To improve the conversion process, we appropriated additional funding for the contractor to make a script which automatically copies the log file data to spreadsheet format daily. The PC has been connected the our plant information network to facilitate periodical data archival and system backups.

#### PEMS INTERFACE TO DCS AND PLANT NETWORK

Unit 22 is equipped with a modern distributed control system (DCS). PEMS collects process data via a DCS interface. Predicted values, along with sensor validation and compliance alarms are transmitted to the DCS for display at the unit operator stations. PEMS data is also communicated to the plant computer network which provides advanced reporting and trending capabilities. The plant network's data is archived for two years, as well as the process log files generated by the PEMS PC to ensure compliance with the Flexible Permit. More interface and DCS configuration details is provided in Appendix 3.

#### CONSIDERATIONS

• Consider the production loss costs and any hydrogen loss costs that will incur during the development of the PEMS model and impacts on any upstream and downstream units.

 Consider whether the unit is capable of running at a steady-state operation for the five or more days per furnace per operating scenario required for PEMS model development.

 Closely follow upcoming federal and state rules regarding compliance monitoring (CAM rule, ACE rule)

· Select operating platform software carefully.

• Make sure that the model outputs are in the format required by the permit or applicable regulations, and ensure that there is adequate hardware to meet the data retention requirements.

 Choose sensors used as model inputs carefully, considering historic reliability of the sensors. If a sensor fails, the PEMS model will run in a sensor validation mode. Failed sensor data reconstruction occurs based on the historic relationship of the failed sensor relative to current values of the other sensors. Sensor validation mode is a good temporary replacement for a failed sensor, however the failed sensor should be repaired as soon as practical.

- Consider the vendor's annual maintenance fees for the models.
- Research and select DCS point configuration carefully.

 Ensure that adequate and proper training, including PEMS theory and other potential process applications, is provided to operations, maintenance and engineering personnel.

#### PERSONNEL CONSIDERATIONS

- Time required for Phillips personnel to assist with initial PEMS implementation, interface and maintenance
  - Production Engineer-150 hours
  - Process Control Engineer-150 hours
  - Process Control Technician-200 hours
  - Computer Maintenance-100 hours
- Sensor repair/replacement and DCS configuration, Instrument Technicians-50 hours
- Recurring maintenance approximate time estimates
  - 25 man-hours per quarter for three PEMS models supporting eight furnaces

<sup>\*</sup> Pavillion Run Time Products is a registered trademark of Pavillion Technologies.

<sup>\*\*</sup> Wonderware InTouch 5 is a registered trademark of Wonderware Inc.

- Four man-hours per sensor of preventative maintenance or replacement as needed
- · Six man-hours per quarter for data backup and archiving
- · One man-hour per week for system checkup and administration.

#### FUTURE DEVELOPEMENTS

The Unit 22 furnaces will be equipped with low NO<sub>x</sub> burners during the next unit turnaround. The models will need to be retrained at this time due to the new burners.

Unit 22 will soon be upgraded to TDC 3000. PEMS will still be interfaced to the system using a PSCI, and the LEPIU will remain. The LEPIU will interface to the TDC 3000 Local Control Network (LCN) through a Highway Gateway.

For our second grandfathered ethylene unit we plan to use *in-situ* analyzers. This type analyzer has the measuring cells in the process as opposed to extractive, where a sample is pulled from the process for an analyzer located elsewhere.

#### APPENDIX 1 Summary of Data Testing Results

#### CONCLUSION

The PEMS model and associated software is a powerful, technologically advanced tool. The PEMS vendor worked with us extensively to meet our needs and to solve any problems. We have not yet realized the cost savings anticipated by selecting a PEMS over a hardware CEMS. We feel this is due partly to the additional regulatory testing requirements placed on a PEMS system and a number of factors unique to our facility such as the wide variability of fuel gas composition and the highly integrated nature of this Ethylene Unit. We have however found the PEMS to be accurate and reliable and are certified and have been in full operation since March 1996.

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#### APPENDIX 2 Breakdown of Process Sensors used.

Model	Furnace	Sensor Ranking	Sensor Most Likely to Affect Concentration of $O_2$	Sensor Most Likely to Affect Formation of NO <sub>x</sub>
1	F-1	1	Stack Oxygen 0.%	Flue Gas Heater Coil Temp
1	F-1	2	Flue Gas Heater Coil Temp	Firebox Temp
i	F-1	3	Stack Gas ID Fan Temp	Stack Oxygen, Os%
í	F-1	4	Firebox Temp	Stack Gas ID Fan Temp
ĩ	F-1	5	Total Fuel Gas Flow	Hydrogen In Fuel Gas, H <sub>2</sub> Mol %
1	F-1	6	Hydrogen in Fuel Gas, H2 Mol %	Total Fuel Gas Flow
1	F-2	1	Stack Oxygen, O <sub>2</sub> %	Firebox Temp
1	F-2	2	Flue Gas Heater Coil Temp	Stack Oxygen, O2%
ĩ	F-2	3	Stack Gas ID Fan Temp	Stack Gas IDFan Temp
ī	F-2	4	Total Fuel Gas Flow	Flue Gas Heater Coil Temp
1	F-2	5	Hydrogen in Fuel Gas, H <sub>2</sub> Mol%	Hydrogen in Fuel Gas, H <sub>2</sub> Mol %
1	F-2	6	Firebox Temp	Total Fuel Gas Flow





F-2, Sensors Most Likely To Affect Formation Of Nox



#### APPENDIX 3

#### DCS Interface/Configuration Details

Unit 22 has a Honeywell TDC 2000\* total distributed control system. Interfacing PEMS to TDC was accomplished using a Honeywell Personal Computer system Interface (PCSI). Once the PCSI connection is made, there are several TDC point types capable of receiving software communications. One method is writing to the setpoint of a Basic Controller. The one we chose is to pass PEMS like a software "mailbox" to the process variable input of a Low Energy Process Interface Unit (LEPIU). We had some difficulty finding enough LEPIU spares to configure all points this way. We purchased a spare point management program, Capacity Analysis Tracking System (CATS2000)\*\* and by using it we were able to find more than enough spares to transmit all model outputs and alarms to LEPIUs. This is important in that the operator will view all the PEMS values as a process variable, instead of a setpoint.

Data is read from and stored to memory of the LEPIU without using a traditional path of field wiring into a multiplexer board. The operational point is configured as a Type 501 (J thermocouple), Conf 7000 (N/A or Off Scan), and Conf Hi Lo 1 – (open thermocouple detection disabled).

One observation worth noting is that some of the operational points can initially display "bad point" errors on the operator consoles. This can be corrected by installing a 250 ohm resistor across the multiplexer card input terminals, temporarily configuring the points to Conf 3000 (On Scan) and setting the points range to 0-100°F; or enough to allow ambient temperature to be scanned in and displayed. The bad point errors clear and configuration can be set back to original settings. In addition, the 250 ohm resistors can be tagged "PEMS", so the terminal will not appear to be spare.

<sup>\*</sup> Honeywell TDC 2000 is a registered trademark of Honeywell Inc.

<sup>\*\*</sup> CATS2000 is a product of Coherent Technologies Inc.

## Kinetics of NO Absorption in Aqueous Iron (II)Thiochelate Solutions

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Ferrous thiochelate solutions were used to absorb NO from flue gas. The absorption rates were studied as a function of pH with a doublestirred reactor at 50° C. The rate constants of five ferrous thiochelates:  $Fe^{2+}(dimercaptosuccinate)_2$ ,  $Fe^{2+}(dithioloxalate)_2$ ,  $Fe^{2+}(aminoethanethiol)_2$ ,  $Fe^{2+}(cysteine)_2$ ,  $Fe^{2+}(penicillamine)_2$ , reacted with NO at pH 5.5 and pH 7.0, have been determined. The implications of the kinetic data on the use of these iron thiochelate additives in wet flue gas desulfurization scrubbers: limestone, lime, and sodium, for simultaneous SO<sub>2</sub> and NO<sub>x</sub> removal is discussed.

#### INTRODUCTION

The aqueous solution of ferrous ions chelated by aminopolycarboxylate, notably ferrous ethylenediaminetetraacetate,  $Fe^{2+}$  (EDTA), has been extensively investigated [1-7] for the absorption of *NO* in flue gas. Despite some promising features []], this type of chelate suffers several drawbacks [3, 8-10]. One of the major drawbacks is the ready oxidation of ferrous chelates [11-13] by flue gas oxygen to ferric chelates, which are incapable of binding *NO*. To circumvent this problem, reducing agents such as sulfite/bisulfite, dithionate, sulfide, ascorbic acid, glyoxal, etc. have been researched to regenerate ferrous chelates. However, none of these reducing agents have produced promising results due to high costs, the slow reduction rate, and/or the production of unwanted by-products.

An alternative approach, using thiochelate, which not only stabilizes the ferrous ions, but also reduces the ferric back to ferrous ions, has been advanced [9,14-17]. In addition to its capacity to rapidly reduce ferric to ferrous ion, through the fast intra-electron transfer process, because of the thiol group attachment to the metal ions; the absorbed *NO* in the ferrous thiochelate solutions unlike the ferrous aminopolycarboxylate system has also been demonstrated to resist reactions with sulfite/bisulfite, which produces unwanted by-products, such as imido sulfates and nitrido sulfates [3,8,14,16,18]. Consequently, the ferrous thiochelate offers simpler scrubber

chemistry, compared with that of the  $Fe^{2*}$  (EDTA) system. In spite of the improvement in scrubber chemistry, the reaction rate of NO in ferrous thiochelate solutions has not been determined. In order to use the laboratory bench-scale results to extraporate the performance of the ferrous thiochelate in a full-size scrubber system [7,9,17], the reaction rate must be obtained.

In this paper, a double stirred reactor with a plane gas-liquid interface was employed to determine the NO absorption rate and secondorder rate constant. The thiochelates investigated were: (1) meso- 2, 3 dimercaptosuccinic acid [ $HO_2CCH(SH)CH(SH)CO_2H$ ]; (2) dithiooxalate [HSCOCOSH]; (3) 2-amino-ethanethiol [ $H_2NCH_2CH_2SH$ ]; (4) L-(+) - cysteine [ $HSCH_2CH(NH_2)CO_2H$ ]; (5) penicillamine [ $(CH_3)_2C(SH)CH(NH_2)CO_2H$ ].

#### EXPERIMENTAL SECTION

#### Materials

Meso-2, 3-dimercaptosuccinic acid (98%, Aldrich); dithioloxalic acid dipotassium salt (Kodak); 2-aminoethanethiol hydrochloride (98%, Aldrich); *L*-(+)-cysteine hydrochloride (MCB) *DL*-penicillamine (Sigma); ferrous sulfate ( $FeSO_4 \cdot 7H_2O$ ; AR grade, Aldrich) were all obtained commercially and used as received. Nitric oxide and sulfur dioxide were obtained from Matheson Co. as a mixture of 2.5% *NO* in  $N_2$  and 0.3%  $SO_2$  in  $N_2$ .

#### Apparatus and procedure

All of the experiments for NO absorption were carried out in a doublestirred reactor with a planar gas-liquid interface. The cell has a water jacket through which water, from a bath kept at a constant temperature, was circulated to maintain the desired temperature. The stirred cell was 8.0 cm in diameter and was equipped with four vertical baffles and two stirring blades. The stirring blades are independent from each other and driven by separate motors. They are used to agitate the gas and liquid phases. Most of the experiments were performed with a liquid stirring speed,  $(n_L)$  150 rpm, and a gas stirring speed,  $(n_G)$  of 900 rpm. A schematic diagram of the apparatus was shown in one of our previous papers [9,10,17].

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The liquid phase was an aqueous solution of  $Fe^{2+}(L)_2$ , where L stands for thiochelates. The  $Fe^{2+}(L)_2$  solution was prepared by adding 1: 2 equimolar amounts of  $FeSO_4.7H_2O$  and ligand to distilled water to make up 10 mM ferrous thiochelate solutions, and the pH of the solution was adjusted by adding aqueous NaOH. The volume of aqueous solution was always set up at 310 ml. Unlike the gas phase, no fresh solution was flowed into the absorber.

The gas phase consisted of NO or SO<sub>2</sub> in nitrogen. 2.5% NO in nitrogen was supplied from a cylinder and was further diluted with  $N_2$  to the desired concentration before being fed to the absorber. The preparation of SO<sub>2</sub> followed the same procedure. The feed concentration of NO ranged from 100 to 600 ppm, and when used, the feed concentration of SO<sub>2</sub> was from 1000 to 2500 ppm. Before the gas mixture was fed into the absorber, it was heated to 50°C and humidified by bubbling through hot water. The absorber was operated with a continuous gas flow of about 1000 mL/min. Gaseous NO was absorbed through the free gas-liquid interface.

A Thermoelectron Model 14A chemiluminescent  $NO_x$  analyzer and a Thermoelectron Model 40 fluorescent  $SO_2$  analyzer were used to monitor the inlet and outlet gas concentrations of NO and  $SO_2$ . A cold trap was used to remove the moisture before the gas entered the analyzers. The concentrations of ferrous and ferric ions were determined by 1,10-phenanthroline colorimetry. The absorption rate was derived from the inlet and outlet gas concentrations, the effective interfacial area, and total gas flow rate. It is reasonable to assume the effective interfacial area is the same as the geometric interfacial area in this type of absorber. The temperature was maintained at 50°C, during the experimental runs, which simulated the temperature in existing FGD scrubbers. The total pressure in the system was 1 atm.

#### Physical properties of $Fe^{2+}(L)_2$ -NO system

The solubility of *NO* in the liquid can be evaluated by the method of van Krevelen and Hoftijzer [19], and the liquid-phase diffusivities of *NO* can be estimated from the equation developed by Wilke and Chang [20]. The concentration of  $Fe^{2*}(L)_2$  was relatively low in our study and the contribution of  $Fe^{2*}(L)_2$  to the total solubility of *NO* is negligible. Some of the parameters for the  $Fe^{2*}(L)_2$ -*NO* system are listed in Table 1.

Table 1. Physical Properties	for Fe <sup>2+</sup> (thioch	elate) <sub>2</sub> -NO System
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Temp. (°C)	[R <sup>2+</sup> (thiochelate) <sub>2</sub> ]	10 <sup>9</sup> D <sub>NO</sub> (m <sup>2</sup> /S)NO	$H_{NO}(atm L mot^{-1})$
25	0.01	2.51	519
50	0.01	4.1	799

#### **RESULTS AND DISCUSSION**

Most of the experimental results obtained from this study are shown as plots of the absorption rate as a function of the interfacial concentration in the liquid phase or other factors. The observed absorption rates of *NO* were converted to chemical reaction enhancement factors using the following equation:

$$N_{A} = k_{GA} (p_{Ao} - p_{Ai}) = k^{\circ}_{LA} E_{A} C_{Ai}$$
(1)

Here, the gas-side and liquid-side mass transfer coefficients,  $k_{GA}$  and  $k^{\rho}_{LA}$ , are obtained from empirical correlations which will be described later.  $C_{Ai}$  is the liquid phase concentration of the gaseous species A at equilibrium with a partial pressure  $P_{Ai}$ . The interfacial concentrations of NO in liquid phase were assumed to be equal to those in water since the concentrations of  $Fe^{2+}(L)_2$  were relatively low at the experimental conditions considered here. The concentration of NO in liquid at the interface was estimated using Henry's law. The outlet concentration of NO was up to 15% lower than the inlet concentration. The values of the inlet and outlet concentrations were averaged to calculate the interfacial NO concentration. While this introduces some uncertainty into the calculations, the results of the measurements using  $Fe^{2+}$  (EDTA) agreed well with values in the literature.

#### Liquid-side and Gas-side Mass Transfer Coefficients

The liquid-side mass transfer coefficient  $(k^{o}_{L})$  of the double-stirred cell was determined by measuring the rate of physical absorption of pure  $CO_{2}$  into water at 25°C, and then correlated with the liquid phase stirring speed,  $n_{L}$ . Under these conditions, the gas-side mass transfer coefficient is unimportant.

$$k^{\circ}_{L,CO2} = 1.635 \times 10^{-6} n_{L}^{0.56} (m / s, 25^{\circ}C)$$
 (2)

The gas-side mass transfer coefficient for the system was determined by absorption of dilute  $SO_2$  into an aqueous 0.5 M NaOH solution and correlated with the gas phase stirring speed,  $n_G$ . Under the conditions for dilute  $SO_2$  absorption into aqueous NaOH solutions, the gas-side mass transfer coefficient determines the transfer rate and the overall mass transfer coefficient is approximately equal to the gas-side mass transfer coefficient,  $K_G=k_G$ 

$$k_{GSO2} = 5.878 \times 10^{-8} n_G^{0.70} (kmol / m^2 \cdot s \cdot kPa, 25^{\circ}C)$$
(3)

The values of liquid-and gas-side mass transfer coefficients for gaseous species I can be calculated by the following correlations involving the diffusivities of the compounds of interest and the experimentally determined values of  $k_{LCO2}$  and  $k_{GSO2}$ , respectively.

$$k^{\circ}_{II} = k^{\circ}_{LCO2} (D_I / D_{CO2})^{2/3}$$
(4)

$$k_{GI} = k_{GSO2} (D_I / D_{SO2})^{2/3}$$
(5)

In our case, the value of  $K_{GNO}$  is 2.36 x 10<sup>-5</sup> kmol/m<sup>2</sup>·s kPa at 150 rpm and 50°C, and  $K_{LNO}$  is 4.60 x 10<sup>-5</sup> m/s at 900 rpm and 50°C.

#### Absorption of NO into Aqueous Solutions

The Henry's constant of NO in water is very small, about  $1.25 \times 10^{-3}$  mol/L'atm at 50°C. However, the complexing reaction in the liquid-phase will enhance the NO solubility dramatically. Nitric oxide reacts with  $Fe^{2*}(L)_2$  to form a nitrosyl complex as follows:

$$NO(g) \stackrel{\sim}{,} NO(aq)$$
 (6)

$$Fe^{2^{*}}(L)_{2}(aq) + NO(aq), Fe^{2^{*}}(L)_{2}(NO)(aq)$$
(7)



FIGURE 1. The effect of pH on the absorption rate of NO by Fe<sup>2+</sup>(DMSA)<sub>2</sub>.

The reactions between the metal chelates and NO should be second order for the forward reaction, i. e., first order in both NO and in metal chelates [4,20]. This must be confirmed experimentally for the ferrousthiochelate system. If the concentration of  $Fe^{2+}(L)_2$  in the bulk liquid,  $C_{BO}$ , is much larger than the concentration of NO at the interface,  $C_{Ai}$ , as satisfied in the present experiments, the kinetics of the reaction becomes pseudo-first order when  $3 < Ha < E_i/2$ , where Ha is the Hatta number, defined by

$$Ha = (D_A k_2 C_{BO})^{1/2} / k_L$$
(8)

and *Ei* is the enhancement factor for instantaneous reaction, defined by

$$E_i = 1 + D_B C_{BO} / z D_A C_{Ai}$$
<sup>(9)</sup>

For the present reaction, the stoichiometric coefficient of *B* is z = 1. If  $D_A = D_B$  and  $C_{B0}/C_{Ai} >> 1$ , then  $E_i = C_{B0}/C_{Ai}$ . Moreover, as Ha > 3, to a close approximation  $E_A = Ha$ , the absorption rate for a pseudomth order reaction is given by

$$N_{A} = \left[ (2 / m + 1) k_{2} C_{Ai}^{m+1} C_{BO} \right]^{1/2}$$
(10)

A plot of log  $N_A$  versus  $C_{Ai}$  gives the reaction order for NO = m; whereas the rate constant  $k_2$  can be determined from  $E_A = Ha$ . Details of the theory have been summarized by Danckwerts [19].



FIGURE 2. The effect of *pH* and the *NO* concentration in liquid at the interface on the absorption rate of *NO* by  $Fet^{2}(DMSA)_{2}$ .



FIGURE 3. The effect of *Pb* on the absorption rate of *NO* by *Fe*<sup>2+</sup> (Dithioloxalate acid)<sub>2</sub>.

#### Rate Measurements and Rate Constants Determination

To determine the forward second-order rate constant of the reaction between NO and ferrous thiochelates, the absorption rate of NO over a range of NO interfacial concentrations in the liquid phase was measured with the stirred reactor and compared with the results for  $R^{2*}(EDTA)$ . Using the mass transfer model described above, the rate constant can then be calculated.

The dimercaptopropane sulfonate [ $HSCH_2CH(SH)CH_2SO_3Na$ ] was previously investigated for the absorption of NO [10]. We have found that the NO absorption rate and rate constants strongly depend on the pH of the solution. The same method was extended here to study other ferrous thiochelate systems. The rate constants of the reaction were measured at the pH of 5.5 and 7.0.

#### (1). Meso2, 3- Dimercaptosuccinic acid (DMSA)

The dimercaptosuccinate is a quadridentate ligand, containing two thiol (-SH) and two carboxylic (-COOH) groups. Ionization of the carboxylic groups facilitates their attachment to ferrous ions, while the thiol groups may coordinate to ferrous ions even without ionization. The pK of two carboxylic and two thiol groups are 2.6, 3.7, 9.4, and 10.6, respectively at an ionic strength of 0.1 at 37°C [22]. The effect of pH on the NO absorption rate by  $Fe^{2+}(DMSA)_2$  is shown in Figure 1. The NO absorption rates increased directly with an increase of pH between 4.0 and 11.0. Beyond pH 11.0, the absorption rate exhibited a slight decrease. Figure 2 shows the changes in NO absorption rate of ion  $Fe^{2+}(DMSA)_2$  as a



FIGURE 4. The effect of pH and NO Absorption rate of Fe<sup>2+</sup> (Dithioloxalate)<sub>2</sub> versus NO liquid interface concentration at different pH.



**FIGURE 5.** The effect of pH on NO absorption rate by  $Fe^{2+}$ (Aminoethanethiol)<sub>2</sub>.

function of the *NO* interface liquid concentration at pH5.5 and 7.0. The results indicate that the *NO* absorption rate at pH7.0 is larger than that at pH5.5. The second order rate constant ( $k_2$ ) can be calculated using the mass transfer model described above,  $k_2 = 3.54 \times 10^7$  l/mol's and 2.76 x 107 l/mol's at pH 7.0 and pH 5.5, respectively.

#### (2). Dithioloxalic Acid

Dithioloxalate is a quadridentate ligand, containing two thiol (-*SH*) and two carbonyl (=*CO*) groups. Unique characteristics of the coordinated dithioloxalate ligand were found, including the ability of the carbonyl groups to function as donors for Lewis acids [23]. The *NO* absorption rate increased directly with *pH* increases from 1.7 to 5.4 (Figure 3). The maximum *NO* absorption rate was at *pH* 5.4. When *pH* was above 5.4, the absorption rate decreased; and at *pH* 10.8, almost no *NO* absorption was detected. Figure 4 depicts the *NO* absorption rate of ferrous dithioloxalate versus the *NO* liquid interface concentration at *pH* 5.5 and 7.0. At the temperature of 50°C, the second order rate constants ( $k_2$ ) are 1.13 x 10<sup>8</sup> l/mol·s and 9.2 x 10<sup>7</sup>1/mol·s at *pH* 5.5 and 7.0, respectively. These kinetic results indicate that the ferrous dithioloxalate is quite a promising additive for use in a wet *SO*<sub>2</sub> scrubber to include *NO* removal. However, the solubility of ferrous dithioloxalate in aqueous solutions is limited, thus restricting its usage in high concentrations.

#### (3). 2- Aminoethanethiol

2-Aminoethanethiol ( $H_2NCH_2CH_2SH$ ) is a bidentate ligand, containing a thiol (-SH) and an amino (-NH<sub>2</sub>) group for the attachment to a metal ion. The *pH* effect on NO absorption rate by ferrous



**FIGURE 6.** The effect of *pH* and aqueous concentration of *NO* at the interface on the absorption rate of *NO* by  $Fe^{2*}(Aminoethanethiol)_2$ .



**FIGURE 7.** The effect of *pH* on the absorption rate of *NO* by  $Fe^{2+}(Cysteine)_2$ .

aminoethanethiol is illustrated in Figure 5. *NO* absorption did not occur at a *pH* of 4.4. The absorption rate increased substantially with the increase of the *pH* from 5.0 to 7.5. Further increase of *pH* from 7.5 to 10.5 resulted in a slight decrease of the absorption rate. Figure 6 depicts the *NO* absorption rate as a function of the *NO* interface concentration at *pH* 5.5 and 7.0. Based on these data, the rate constants  $(k_2)$  at  $50^{\circ}$ C are calculated to be  $5.75 \times 10^3$  1/mol's and 2.95  $\times$  10<sup>7</sup> 1/mol's at pH 5.5 and 7.0, respectively. A low rate constant at *pH* 5.5 indicates that 2-Aminoethanethiol is not suitable for use in a limestone FGD system, which operates at a *pH* between 5 and 6.

#### (4). L-(+)-Cysteine

Cysteine is a tridentate ligand containing a thiol (-SH), an amino (-NH<sub>2</sub>), and a carboxyl (-COO') groups, which may facilitate the coordination of ferrous ions. The *pK* of the carboxylic and thiol groups in cysteine [24] are 2.12 and 10.38, respectively. The effect of *pH* on the absorption rate of *NO* by ferrous cysteine is shown in Figure 7. The *NO* absorption rate increased rapidly as the *pH* increased from *pH* 5.5 to 7.0. When *pH* is increased beyond 7.0, the *NO* absorption rate of ferrous cysteine versus the *NO* interface liquid concentration at *pH* 5.5 and 7.0 are illustrated in Figure 8. Based on these results, the second-order rate constant ( $k_2$ ) has been calculated: 8.73 x10<sup>5</sup> *V*mol's at *pH* 5.5, and 4.6 x 10<sup>7</sup> *V*mol's at *pH* 7.0.

#### (5). DL - Penicillamine

Penicillamine is similar to cysteine, a tridentate ligand having a thiol (-SH), an amino (- $NH_2$ ), and a carboxyl (- $COO^{-}$ ) groups. The NO absorption rate of ferrous penicillamine is also affected by pH (Figure 9). The absorption



**FIGURE 8.** The effect of pH and NO absorption rate of  $Fe^{2+}(Cysteine)_2$  versus NO interface liquid concentration.



**FIGURE 9.** The effect of pH on the absorption rate of NO by  $Fe^{2+}$ (Penicillamine)<sub>2</sub>.

rate increased along with the increase of pH from 4.0 to 7.0. The rate slightly decreased with a further increase of pH above 7.0. Figure 10 depicts the results of *NO* absorption rate increase with the increase of *NO* liquid interface concentration at pH 5.5 and 7.0. The rate constants (k<sub>2</sub>) can be calculated: 5.18 x 10<sup>6</sup> 1/mol's and 4.42 x 10<sup>7</sup> 1/mol's at pH 5.5 and 7.0, respectively.

In summary, the second order rate constants determined for the five ferrous thiochelates discussed above is shown in Table 2.

#### CONCLUSIONS

The experimental results indicate that *NO* absorption rates and rate constants are strongly influenced by the pH of the ferrous thiochelate solutions. The second order rate constants of the reaction between *NO* and five types of ferrous thiochelates have been determined at 50°C. The rate constants appear in Table 2.

Previously [10], we determined the rate constant of *NO* absorption by *Fe*<sup>2+</sup>(DMPS)<sub>2</sub> (where DMPS is dimercapto propanesulfonate) to be 1.1 x 10<sup>7</sup> *l*/mol's and 1.1 x10<sup>8</sup> *l*/mol's at pH 5.2 and 7.2, respectively, at 50°C. Judging from the results obtained so fat, it appears that, based on the kinetic point of view, the order of suitability for use in a wet limestone system, where the *pH* of the scrubbing liquor normally ranges between 5 and 6, are: *Fe*<sup>2+</sup>(dithioloxalate)<sub>2</sub>> *Fe*<sup>2+</sup>(DMSA)<sub>2</sub> > *Fe*<sup>2+</sup>(DMPS)<sub>2</sub> > *Fe*<sup>2+</sup>(emicillamine)<sub>2</sub>> *Fe*<sup>2+</sup>(cysteine)<sub>2</sub>> *Fe*<sup>2+</sup>(aminoethanethiol)<sub>2</sub>. On the other hand, in a wet lime stone system, where the *pH* of the liquor (the *pH* can be larger than 6.5) is higher than that in a wet limestone system, a the order becomes : *Fe*<sup>2+</sup>(DMPS)<sub>2</sub> > *Fe*<sup>2+</sup>(dithioloxalate)<sub>2</sub>> *Fe*<sup>2+</sup>(dithioloxalate)<sub>2</sub>> *Fe*<sup>2+</sup>(cysteine)<sub>2</sub>> *Fe*<sup>2+</sup>(emicillamine)<sub>2</sub>> *Fe*<sup>2+</sup>(DMSA)<sub>2</sub> > *Fe*<sup>2+</sup>(dithioloxalate)<sub>2</sub>> *Fe*<sup>2+</sup>(furthioloxalate)<sub>2</sub>> *Fe*<sup>2+</sup>(furthioloxalate)<sub>2</sub>> *Fe*<sup>2+</sup>(furthioloxalate)<sub>2</sub>> *Fe*<sup>2+</sup>(firthioloxalate)<sub>2</sub>> *Fe*<sup>2+</sup>(firthiol



**FIGURE 10.** The effect of *pH* absorption rate of *Fe*<sup>2+</sup> (Penicillamine)<sub>2</sub> No liquid interface concentration.

#### Table 2. Second Order Rate Constant of the Reaction Between NO and Ferrous Thiochelates.

COMPOUND	Rate at <i>pH</i> 5.5 (1/mol·s)	Rate at pH7.0 (1/mol·s)
Fe <sup>2+</sup> (DMSA) <sub>2</sub>	2.76 x 10 <sup>7</sup>	3.45 x 10 <sup>7</sup>
Fe 2+(dithioloxalate)2	1.13 x 10 <sup>8</sup>	9.2 x 10 <sup>7</sup>
$Fe^{2+}(aminoethanethiol)_2$	5.75 x 10 <sup>3</sup>	2.95 x 10 <sup>7</sup>
Fe <sup>2+</sup> (cysteine) <sub>2</sub>	8.73 x 10 <sup>5</sup>	4.6 x 10 <sup>7</sup>
Fe <sup>2+</sup> (penicillamine) <sub>2</sub>	5.18 x 10 <sup>6</sup>	4.42 x 10 <sup>7</sup>

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#### NOMENCLATURE

- C =liquid phase concentration, mol/L [1 mol/L = 10<sup>3</sup> mol/m<sup>3</sup>]
- D = molecular diffusivity, m<sup>2</sup>/s
- *E* = enhancement factor for absorption with chemical reaction, dimensionless
- H = Henry's Law constant, M atm<sup>-1</sup>
- Ha = Hatta number,  $(D_A k_2 C_{B0})^{1/2} k_L$
- $k_2$  = second-order forward rate constant, L/mol s
- $k_{\rm G}$  = gas phase mass transfer coefficient, kmol/m<sup>2</sup>s kPa
- $k_{\rm I}$  = liquid phase mass transfer coefficient, m/s
- m = reaction order
- $N_{\rm A}$ = absorption rate, mol/m<sup>2</sup>s
- $n_{\rm G}$  = gas phase stirrer speed, rpm
- $n_{\rm L}$  = liquid phase stirrer speed, rpm
- p = partial pressure, kPa
- z = stoichiometric coefficient

#### Subscripts

#### A=NO

- B = absorbent in liquid phase
- i = gas-liquid interface
- 0= bulk liquid

#### Superscripts

<sup>0</sup> = without chemical reaction

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